

CHEMICAL REFINING *of* PETROLEUM

The Action of Various Refining Agents and
Chemicals on Petroleum and its Products

By

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Revised Edition



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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, secretary of the society, Washington, D. C.; the late John E. Teeple, then treasurer of the society, New York; and Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A. C. S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed editors (the present list of whom appears at the close of this introduction) to have charge of securing authors, and of considering critically the manuscripts submitted. The editors endeavor to select topics of current interest, and authors recognized as authorities in their respective fields.

The development of knowledge in all branches of science, especially in chemistry, has been so rapid during the last fifty years, and the fields covered by this development so varied that it is difficult for any individual to keep in touch with progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and by such compendia as Beilstein's *Handbuch der Organischen Chemie*, Richter's *Lexikon*, Ostwald's *Lehrbuch der Allgemeinen Chemie*, Abegg's and Gmelin-Kraut's *Handbuch der Anorganischen Chemie*, Moissan's *Traité de Chimie Minérale Générale*, Friend's and Mellor's Textbooks of Inorganic Chemistry and Heilbron's Dictionary of Organic Compounds, it often takes a great deal of

time to coördinate the knowledge on a given topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value. It was with a clear recognition of the usefulness of such work that the American Chemical Society undertook to sponsor the publication of the two series of monographs.

Two distinct purposes are served by these monographs: the first, whose fulfillment probably renders to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a form intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs enable such men to form closer contact with work in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made, and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, extended references to the literature enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection is made of those papers which are most important.

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Preface to the First Edition

The purpose of this volume is to present the theory and practice of the various chemical processes used in refining petroleum and its products and in improving certain desirable characteristics of the finished products.

With the increasing demand for better petroleum products and preparation at the least possible cost, a bewildering array of chemical refining and treating processes has been proposed by the many chemists working in this field. Some of these processes have proved highly successful; most of them are of questionable value; and doubtless many others only await modification and further improvement to become practicable. The literature of the subject is extensive. It is scattered throughout a great variety of books, periodicals, and patent specifications in many countries and represents the labor not only of individuals but of scientific institutions and staffs of the major petroleum companies. This treatise offers in one volume the data and results of investigations in chemical refining and the use of various reagents in the improvement of petroleum products, collected from the different sources so that the information on this subject may be readily available. The patent literature, whether or not the patents are still in force, often presents valuable detailed information on processes and operations. Those patents of immediate application are discussed in the different chapters of the text in connection with their proper subject, and others recently issued or that seem somewhat less closely allied to the subject are classified at the end of the book according to chapter headings.

The authors have discussed more or less in detail those investigations and processes which their own experience in petroleum technology has shown to be of practical importance. They have also included briefer comments on many proposed processes of somewhat questionable value in order to present a complete record of the subject. Because of the complexity of the constituents of any one sample of petroleum and the difference in composition of crude oils from various sources, and because of the frequent changes in the desired qualities sought in the finished products, a refining process found suitable for one oil may be inadequate for another, or a process considered suitable at one time for a given product may be obsolete a few years later with the development of more data and information. These factors must always be considered by investigators in the application of any chemical to petroleum.

The publication of this book is the result of the combined efforts of the coauthors, who for many years in close cooperation have collected the

materials from the literature and from their own experience. The book in its final form represents the joint opinions of both authors.

The authors wish to acknowledge their indebtedness to Dr. Herbert N. McCoy, who has read the entire manuscript and offered a great many helpful criticisms; to Dr. W. F. Faragher of the Vacuum Oil Company, Inc., for his valuable technical criticisms of the whole manuscript; to Philip S. Clarke of the Research Department of the Union Oil Company of California for his criticism of the chapter on Adsorbents; to the Union Oil Company of California, especially W. L. Stewart, Jr., Vice President, and R. E. Haylett, Director of Manufacturing, for the privilege of using some of the important experimental data; to Dr. H. A. Curtis, Manager of the Research and Development Department of the Vacuum Oil Company, Inc., for many helpful suggestions; and to the many others who are mentioned in the pages of the book who have so kindly permitted the use of the data and results of their work. The authors are especially grateful to Bertha C. Stagner for much patient assistance in the critical preparation of the manuscript and in reviewing the proof sheets, and to Kira V. Kalichevsky for valuable assistance in the compilation of references and indexes.

The Authors.

Preface to the Revised Edition

As the first edition of this book, which was exhausted two years ago, met a favorable response from petroleum technologists, the authors believe that a revised edition should now be published which will include investigations and processes developed since the publication of the first edition seven years ago. With this object in view, the whole book has been revised, and much of it entirely rewritten. The patent literature of the first edition proved to be of value, and a more nearly complete supplementary list of the United States patents not already discussed in the text has been added. For various reasons the foreign patents have not been added to this supplementary list.

The authors wish to express their appreciation to J. B. Rather and to others whose names appear in the book for assistance with information on special subjects and for permission to use data from investigations and publications.

The Authors.



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Chapter I

Composition of Petroleum

Crude petroleum is composed of various types of hydrocarbons, and small proportions of combined sulfur, oxygen, and nitrogen are usually present. The total percentage of sulfur, oxygen, and nitrogen varies from almost zero to about four or five per cent, or higher in very rare cases. In addition, the crude oil may contain inorganic constituents in amounts varying from mere traces to a few hundredths of a per cent; these are presumably oil-soluble salts of the petroleum acids, or salts in solution in the water emulsified in the oil. The water actually in solution in oil is not over 0.01 per cent of the volume of the oil. The water-in-oil emulsions are believed not to exist in nature but to be formed in the wells. Crude petroleum, when brought to the surface, may contain as much as 10 to 30 per cent of emulsified water, and in certain fields even 50 per cent or more. Such oils are dehydrated before they are shipped to the refineries.*

CLASSIFICATION OF CRUDE OILS

The fact that the properties of crude petroleum vary widely makes their classification very difficult. Even crude oils obtained from different wells in the same field may show considerable variation in their properties. All crude oils are not capable of yielding the desired finished products, and refining methods vary with the character of the crude oil available. However, classification of petroleum is important.

In the most generally accepted classification of crude petroleum, though not the best, there are three divisions: paraffin-base, mixed-base, and asphalt-base crude oils. This classification is based primarily on the relative quantities of paraffin wax and asphalt in the crude oil. The paraffinic petroleum, such as those of Pennsylvania, contain large amounts of paraffin wax and practically no asphalt; the mixed-base petroleum, such as those of the Mid-Continent, contain both paraffin wax and asphalt; and the asphalt-base petroleum, such as those of the Gulf Coast and California, contain asphalt but almost no paraffin wax. This classification is faulty because it takes into consideration only the presence of certain types of substances in the crude oil, and these substances do not necessarily indi-

*Dow²³ gives a comprehensive survey of the various dehydrating methods now in use. See also Berkman and Egloff, "Emulsions and Foams," New York, Reinhold Publishing Corp., 1941.

cate the nature of other important constituents. The impossibility of predicting the properties of the distillation fractions from the content of asphalt or wax in the crude oil is well illustrated by the following example. Rodessa, Louisiana, petroleum contains both asphalt and wax and should, therefore, be classified as a mixed-base crude oil. The distillation fractions from this oil possess certain properties, however, which are considered to be associated only with petroleum of highly paraffinic nature. Petroleums such as those of California, Russia, or Borneo are even more difficult to classify, as their distillation fractions differ widely from those commonly associated with the petroleums of asphaltic, mixed, and paraffinic types.

Another system classifies the crude petroleums according to the preponderance of one or another class of hydrocarbons.⁶⁸ This system recognizes the existence of the following types of petroleum:

- (1) methane
- (2) naphthene
- (3) methane-naphthene
- (4) aromatic
- (5) methane-naphthene-aromatic
- (6) naphthene-aromatic

Types 1, 2, and 3 are characterized by the presence of only small proportions of polycyclic compounds, and by long chains or side chains; type 4, a very rare crude oil, is purely aromatic, with a prevalence of aromatic compounds in all fractions, and it has a high specific gravity; type 5 has a preponderance of polycyclic aromatic compounds and naphthenes; and type 6 has a highly complicated ring structure, and the side chains are very short. This classification, although preferable to the previous one, does not take into account the change in the composition of the different distillation fractions of the crude oil that occurs from the lighter to the heavier fractions. The classification is, therefore, unsatisfactory.

Still another classification has recently been proposed, according to which the first term of the compound adjectives refers to light fractions, and the second term to heavy fractions in the crude oil.⁴³ The following types of crude petroleums are thus differentiated:

- (1) paraffin base
- (2) paraffin-intermediate base
- (3) intermediate-paraffin base
- (4) intermediate base
- (5) intermediate-naphthene base
- (6) naphthene-intermediate base
- (7) naphthene base

- (8) paraffin-naphthene base (analysis not known)
- (9) naphthene-paraffin base (analysis not known)

It seems doubtful whether this classification is entirely adequate, as certain crude petroleum may differ from one another not only in the nature of light and heavy fractions but also in the nature of the residuum. Each division of the classification would, therefore, require the use of compound adjectives containing more than two terms, and would thus become very cumbersome. The boiling point and viscosity distribution curves are also different for different crude petroleum, and these require further definitions for the so-called light and heavy fractions, irrespective of the characteristics of individual crude oils.

Since there are obvious objections to each of the classifications proposed, it appears questionable whether a concise and satisfactory system for classifying the crude petroleum can be developed; and as the first system is the simplest and the most widely accepted, it will be used in this book whenever possible.

CHEMICAL COMPOSITION OF PETROLEUM

As stated above, the principal constituents of petroleum are compounds of carbon and hydrogen. The percentages of carbon and hydrogen in petroleum from all parts of the world do not vary over a wide range, the percentage of carbon being from 83 to 87, and that of hydrogen from 11 to 14. However, the ultimate analysis of different petroleum gives but little indication of their extremely varied physical and chemical characteristics.

Crude petroleum are composed for the most part of the following series or classes of compounds: paraffins; naphthenes; aromatics; possibly, in addition, very small proportions of olefins, or unsaturated hydrocarbons; and generally a high percentage of asphaltic matter, which is composed of hydrocarbon substances containing a relatively small percentage of hydrogen. The chemical structure of the asphalt is not known. The percentage of olefins in cracked products may be high—15 to 45, or even higher; but it is generally accepted that if olefins had occurred at any time in crude oil, they would have been extensively polymerized by their long contact with the silicious material of the earth.

The crude petroleum may consist not only of a mutual solution of these series of compounds but of combinations of radicals from two or more different hydrocarbon series. For example, a molecule may be made up of a naphthene or aromatic nucleus with side chains belonging to the paraffin series; or, as is generally assumed, different types of ring nuclei may be grouped together in the same molecule. The proportions of the

individual series of hydrocarbons present, as well as the extent to which the individual members of any one series are present, make enormous differences in the properties of crude oils. For illustration, some of the wells in the Kettleman Hills of California yield crude oil containing from 50 to 90 per cent of hydrocarbons boiling below 425° F. (gasoline), whereas wells in other oil fields of California produce petroleum containing as little as one or two per cent of constituents boiling below 425° F. For corresponding but more detailed data on hundreds of different samples of crude oil, the reader should consult other publications.¹⁹

The results of the chemical examinations of the Pennsylvania petroleum products in the early history of the American industry largely account for the somewhat general opinion that the percentage of aliphatic hydrocarbons in all crude oils is much higher than it really is. The naphthenes doubtless occur in all petroleum; and although the percentages are variable, the average is greater than that of the paraffins. The two series are much less reactive toward the usual chemical reagents than any of the other known hydrocarbons. Gruse³⁶ points out that though there is very little information on the true percentages of paraffin hydrocarbons present in oils from different fields, it appears from Mabery's work on the Pennsylvania gasolines and kerosenes that perhaps 30 to 40 per cent of the Pennsylvania crude oil is paraffinic. In contrast with this crude oil, the asphaltic and naphthenic oils, such as some of those of the Gulf Coast, may contain practically no paraffins in either the low- or high-boiling fractions. The low-boiling fractions of Baku crude oil contain from 80 to 90 per cent of naphthenes, and some of the Ohio and Canadian crude oil fractions boiling above 400° F. seem to be two-thirds naphthenes. Much of the crude oil from Borneo is exceptional in being very rich in aromatic hydrocarbons (25 to 40 per cent), and of this aromatic content six to seven per cent belongs to the naphthalene series. Other data show that the kerosene fractions of the Mid-Continent petroleum consist primarily of naphthenes, whereas much of the kerosene of California consists of naphthenes with varying proportions of aromatic and paraffinic hydrocarbons. Egloff, Bollman, and Levinson²⁶ assume that on an average at least one-fourth of all crude oil is made up of naphthenic hydrocarbons.

Because of the complexity of hydrocarbons present in petroleum, it seems preferable to express their composition in terms of hydrocarbon radicals or nuclei rather than of the classes of hydrocarbons present; otherwise, for example, a molecule with a naphthene or an aromatic group with a very long side chain might be more closely related chemically to a paraffin than to a naphthene or aromatic, and would thus be classified as paraffinic. Attempts to classify petroleum hydrocarbons into distinctly

different classes of compounds also create an impression that there is a discontinuity in common properties of the successive petroleum fractions. Such discontinuity exists in the most volatile portions of the crude oil, but disappears in its heavier portions. This continuity may be explained by the presence in the crude oil of a very large number of substances which form an uninterrupted chain of compounds; the individual members of this chain differ only a little from one another in their properties, the physical data of which actually overlap at times.

The following discussion is restricted to a brief description of the different series of hydrocarbons and other substances found in petroleum. Discussion of chemistry readily available in general treatises on organic chemistry is purposely omitted, except when necessary for clarity. Tabulations are included of some of the members of the important classes or series of hydrocarbons occurring in petroleum.⁷¹ Although all special individual members listed in the tables have not been isolated from petroleum, they are, nevertheless, representative of the hydrocarbons found; and such tabulations are a source of convenience in making comparisons between petroleum products and the known chemical individuals. It is further stressed that although much work has been done on the composition of petroleum, little is known of its chemical structure because of the complexity of these hydrocarbons and the impossibility of devising reliable and quick methods for their analysis.

Paraffin Hydrocarbons (C_nH_{2n+2})

Some of the individual paraffin hydrocarbons are shown in Table 1. At normal temperatures all the members of this series below pentane are gases; those between pentane and pentadecane ($C_{15}H_{32}$) are liquids; and those above pentadecane are waxy solids. The straight-chain, or normal, paraffin hydrocarbons have been synthesized up to and including the molecules containing 70 carbon atoms and melting at 221° F. (105° C.).⁷⁷ Table 1 includes the isomers of butane, pentane, hexane, heptane, and several of octane, but only the normal paraffins from octane on. All of the theoretically possible isomers of butane, pentane, and hexane, four of the nine heptanes, nine of the eighteen octanes, six of the thirty-five nonanes, the normal, or straight-chain, decane, undecane, and dodecane have certainly been isolated from petroleum in substantially pure form.⁶² The actual percentages of these different hydrocarbons present in petroleum are small, as shown by the results of the above investigations.

Individual hydrocarbons up to $C_{35}H_{72}$ have been reported in paraffin oil and paraffin wax, but it is possible that the investigators were not dealing with pure compounds. The large number of possible isomers (see Table 7) in the large molecules and their physical similarities make the

Table 1. Paraffin Hydrocarbons.

	Formula	Melting Point (°F.) (°C.)		Boiling Point ^a (°F.) (°C.)		Sp. Gr. at °C.
Methane	CH ₄	-300	-184	-258.5	-161.4	0.415 (liq. -164°)
Ethane	C ₂ H ₆	-278	-172	-126.4	-88.3	0.446 (liq. 0°)
Propane	C ₃ H ₈	-309.8	-189.9	-48.1	-44.5	0.536 (liq. 0°)
Butanes						
<i>n</i> -Butane	C ₄ H ₁₀	-211.8	-135	31	-0.6	0.60 (0°)
Isobutane	C ₄ H ₁₀	-229	-145	13.6	-10.2	0.559 (20°)
Pentanes						
<i>n</i> -Pentane	C ₅ H ₁₂	-201.7	-129.9	96.8	36	0.626 (20°)
Isopentane (2-methylbutane)	C ₅ H ₁₂	-254.8	-159.7	87.8	28	0.619 (20°)
2,2-Dimethylpropane	C ₅ H ₁₂	-4	-20	49.1	9.5	0.613 (0°)
Hexanes						
<i>n</i> -Hexane	C ₆ H ₁₄	-139.5	-95.3	155.7	68.7	0.660 (20°)
Isohexane (2-methylpentane)	C ₆ H ₁₄	-244.6	-153.7	140.4	60.2	0.654 (20°)
3-Methylpentane	C ₆ H ₁₄	-180.4	-118	145.8	63.2	0.668 (20°)
2,3-Dimethylbutane	C ₆ H ₁₄	-144.8	-98.2	121.5	49.7	0.649 (20°)
2,3-Dimethylbutane	C ₆ H ₁₄	-211.2	-135.1	136.6	58.1	0.662 (20°)
Heptanes						
<i>n</i> -Heptane	C ₇ H ₁₆	-130.9	-90.5	209.1	98.4	0.684 (20°)
Isoheptane (2-methylhexane)	C ₇ H ₁₆	-182.4	-119.1	194	90	0.679 (20°)
3-Methylhexane	C ₇ H ₁₆	-182.9	-119.4	197.2	91.8	0.687 (20°)
3-Ethylpentane	C ₇ H ₁₆	-181.8	-118.8	199.9	93.3	0.698 (20°)
2,2-Dimethylpentane	C ₇ H ₁₆	-194.1	-125.6	174	78.9	0.674 (20°)
2,3-Dimethylpentane	C ₇ H ₁₆			193.5	89.7	0.695 (20°)
2,4-Dimethylpentane	C ₇ H ₁₆	-182.9	-119.4	177.4	80.8	0.675 (20°)
3,3-Dimethylpentane	C ₇ H ₁₆	-211	-135	186.8	86	0.693 (20°)
2,2,3-Trimethylbutane	C ₇ H ₁₆	-13	-25	177.6	80.9	0.690 (20°)
Octanes						
<i>n</i> -Octane	C ₈ H ₁₈	-70.4	-56.9	258.1	125.6	0.703 (20°)
Isooctane (2-methylheptane)	C ₈ H ₁₈	-168.3	-111.3	243	117.2	0.698 (20°)
2,2,4-Trimethylpentane ^b	C ₈ H ₁₈	-160.3	-107.4	210.7	99.3	0.692 (20°)
<i>n</i> -Nonane	C ₉ H ₂₀	-64.7	-53.7	303.3	150.7	0.718 (20°)
<i>n</i> -Decane	C ₁₀ H ₂₂	-21.5	-29.7	345.2	174	0.730 (20°)
<i>n</i> -Undecane	C ₁₁ H ₂₄	-14.3	-25.7	384.4	195.8	0.740 (20°)
<i>n</i> -Dodecane	C ₁₂ H ₂₆	14.4	-9.7	420.6	216.2	0.749 (20°)
<i>n</i> -Tridecane	C ₁₃ H ₂₈	21.2	-6	453.2	234	0.772 (0°)
<i>n</i> -Tetradecane	C ₁₄ H ₃₀	41.9	5.5	486.5	252.5	0.774 (at m.p.)
<i>n</i> -Pentadecane	C ₁₅ H ₃₂	50	10	518.9	270.5	0.776 (at m.p.)
<i>n</i> -Hexadecane (cetane)	C ₁₆ H ₃₄	64.4	18	549.5	287.5	0.775 (at m.p.)
<i>n</i> -Heptadecane	C ₁₇ H ₃₆	72.5	22.5	577.4	303	0.777 (at m.p.)
<i>n</i> -Octadecane	C ₁₈ H ₃₈	82.4	28	602.6	317	0.777 (at m.p.)
<i>n</i> -Nonadecane	C ₁₉ H ₄₀	89.6	32	626	330	0.777 (at m.p.)
<i>n</i> -Eicosane	C ₂₀ H ₄₂	97.7	36.5	401	205	0.778 (at m.p.)
					(15 mm.)	
<i>n</i> -Heneicosane	C ₂₁ H ₄₄	104.9	40.5	419	215	0.778 (at m.p.)
					(15 mm.)	
<i>n</i> -Docosane	C ₂₂ H ₄₆	111.9	44.4	436.1	224.5	0.778 (at m.p.)
					(15 mm.)	
<i>n</i> -Tricosane	C ₂₃ H ₄₈	117.8	47.7	453.2	234	0.778 (at m.p.)
					(15 mm.)	
<i>n</i> -Tetracosane	C ₂₄ H ₅₀	123.8	51	465.2	324	0.779 (at m.p.)
<i>n</i> -Pentacosane	C ₂₅ H ₅₂	129.2	54	761	405	0.779 (20°)
<i>n</i> -Hexacosane	C ₂₆ H ₅₄	134.6	57	784.4	418	0.779 (20°)
<i>n</i> -Heptacosane	C ₂₇ H ₅₆	139.1	59.5	518	270	0.780 (at m.p.)
					(15 mm.)	

^a At 760 mm. mercury unless otherwise specified.^b This chemical used as standard in octane rating.

Table 1. Paraffin Hydrocarbons.—*Continued.*

	Formula	Melting Point (°F.) (°C.)		Boiling Point ^a (°F.) (°C.)		Sp. Gr. at °C.
<i>n</i> -Octacosane	C ₂₈ H ₅₈	143.6	62	834.8	446	0.779 (20°)
<i>n</i> -Nonacosane	C ₂₉ H ₆₀	146.3	63.5	896	480	0.780 (20°)
<i>n</i> -Triacontane	C ₃₀ H ₆₂	150.8	66	861.8	461	0.780 (20°)
<i>n</i> -Hentriacontane	C ₃₁ H ₆₄	154.6	68.1	575.6	302	0.781 (at m.p.)
				(15 mm.)		
<i>n</i> -Dotriacontane (dicetyl)	C ₃₂ H ₆₆	158	70	590	310	0.773 (80°)
				(15 mm.)		
<i>n</i> -Tritriacontane	C ₃₃ H ₆₈	161.6	72	622.4	328	0.780 (at m.p.)
				(15 mm.)		
<i>n</i> -Tettracontane	C ₃₄ H ₇₀	163.4	73	908.6	487	0.780 (at m.p.)
<i>n</i> -Pentatriacontane	C ₃₅ H ₇₂	166.5	74.7	627.8	331	0.782 (at m.p.)
				(15 mm.)		
<i>n</i> -Hexatriacontane	C ₃₆ H ₇₄	168.8	76	509	265	0.782 (at m.p.)
				(1.0 mm.)		
<i>n</i> -Tetracontane	C ₄₀ H ₈₂	177.8	81	465.8	241	
				(0.3 mm.)		
<i>n</i> -Pentacontane	C ₅₀ H ₁₀₂	199.4	93	789.8	421	0.794 (at m.p.)
				(15 mm.)		
<i>n</i> -Hexacontane	C ₆₀ H ₁₂₂	210.2	99			
<i>n</i> -Dohexacontane	C ₆₂ H ₁₂₆	213.8	101			
<i>n</i> -Tetrahexacontane	C ₆₁ H ₁₂₆	215.6	102			
<i>n</i> -Heptacontane	C ₇₀ H ₁₄₂	221	105			

isolation of individual isomers almost hopeless, although it is doubtful whether a large number of all the possible isomers actually exists in the oil.

The paraffin hydrocarbons which boil at the same temperatures as the lubricating oil fractions are solid waxes at normal temperatures and are purposely removed from the lubricating oil distillates. If these were not removed, the lubricating oil could not be kept mobile when moderately cool. It will be noted later, however, that the addition of small quantities of certain chemicals lessens the tendency of the wax to separate.

Naphthene Hydrocarbons (C_nH_{2n})

Naphthenes are saturated hydrocarbons corresponding to the formula C_nH_{2n}. They are made up of closed rings of methylene groups and may have side chains of various groupings. Cyclohexane is a typical naphthene.

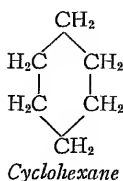


Table 2 contains many members of the naphthene series up to and including those with 12 carbon atoms. The first compound shown in the table, cyclopropane, has not been found associated with petroleum, and as yet there is uncertainty about the presence of the second, cyclobutane. Cyclopentane, cyclohexane, and several of their simpler alkyl-substituted

Table 2. Naphthene Hydrocarbons.

Name	Formula	Melting Point (°F.)	Melting Point (°C.)	Boiling Point at 760 mm. (°F.)	Boiling Point at 760 mm. (°C.)	Sp. Gr. at °C.
Cyclopropane	C_3H_6	-195.9	-126.6	-29.9	-34.4	0.720 (-79°)
Methylcyclopropane	$CH_3 \cdot C_3H_5$			41	5	0.691 (-20°)
1,1-Dimethylcyclopropane	$(CH_3)_2 \cdot C_3H_4$			69.8	21	0.660 (20°)
1,1,2-Trimethylcyclopropane	$(CH_3)_3 \cdot C_3H_3$			127	52.8	0.695 (20°)
1,2,3-Trimethylcyclopropane	$(CH_3)_3 \cdot C_3H_3$			149	65	0.692 (22°)
Cyclobutane	C_4H_8	-58	-50	55.4	13	0.703 (0°)
Methylcyclobutane	$CH_3 \cdot C_4H_7$			107.6	42	0.694 (20°)
Ethylcyclobutane	$C_2H_5 \cdot C_4H_7$			161.6	72	0.745 (20°)
3-Cyclobutylpentane	$C_3H_7 \cdot CH(C_4H_7) \cdot C_5H_{12}$			303.8-309.2	151	0.795 (19°)
Cyclopentane	C_5H_{10}	-135.9	-93.3	122	50	0.751 (20°)
Methylcyclopentane	$CH_3 \cdot C_5H_9$	-220.9	-140.5	161.6	72	0.750 (20°)
1,1-Dimethylcyclopentane	$(CH_3)_2 \cdot C_5H_8$			189.5	87.5	0.755 (20°)
1,2-Dimethylcyclopentane	$(CH_3)_2 \cdot C_5H_8$			197.6	92	0.753 (20°)
1,3-Dimethylcyclopentane	$(CH_3)_2 \cdot C_5H_8$			195.8	91	0.754 (20°)
1-Methyl-2-ethylcyclopentane	$(CH_3)(C_2H_5) \cdot C_5H_8$			255.2	124	0.754 (20°)
1-Methyl-3-ethylcyclopentane	$(CH_3)(C_2H_5) \cdot C_5H_8$			249.8	121	0.764 (20°)
Cyclohexane	C_6H_{12}	43.7	6.5	178.5	81.4	0.779 (20°)
Methylcyclohexane	$CH_3 \cdot C_6H_{11}$	-195.3	-126.3	213.4	100.8	0.770 (20°)
1,1-Dimethylcyclohexane	$(CH_3)_2 \cdot C_6H_{10}$	-71.5	-57.5	248	120	0.779 (20°)
1,2-Dimethylcyclohexane	$(CH_3)_2 \cdot C_6H_{10}$			254.2	124	0.771 (20°)
1,3-Dimethylcyclohexane	$(CH_3)_2 \cdot C_6H_{10}$			249.8	120.5	0.769 (20°)
1,4-Dimethylcyclohexane	$(CH_3)_2 \cdot C_6H_{10}$	-122.8	-86	248	120	0.766 (20°)
Ethylcyclohexane	$C_2H_5 \cdot C_6H_{11}$			266	130	0.777 (20°)
1,1,3-Trimethylcyclohexane	$(CH_3)_3 \cdot C_6H_9$			280.4	138	0.790 (20°)
1,2,4-Trimethylcyclohexane	$(CH_3)_3 \cdot C_6H_9$			284	287.6	0.778 (20°)
1,3,5-Trimethylcyclohexane	$(CH_3)_3 \cdot C_6H_9$			278.6-282.2	137-9	0.772 (20°)
1-Methyl-2-ethylcyclohexane	$(CH_3)(C_2H_5) \cdot C_6H_{10}$			303.8	151	0.784 (20°)
1-Methyl-3-ethylcyclohexane	$(CH_3)(C_2H_5) \cdot C_6H_{10}$			300.2	149	0.799 (20°)
1-Methyl-4-ethylcyclohexane	$(CH_3)(C_2H_5) \cdot C_6H_{10}$			302	150	0.804 (0°)
Propylcyclohexane	$C_3H_7 \cdot C_6H_{11}$			301.1	149.5	0.767 (20°)
Isopropylcyclohexane	$C_3H_7 \cdot C_6H_{11}$			302	150	0.787 (20°)
1-Methyl-4-isopropylcyclohexane	$(CH_3)(C_3H_7) \cdot C_6H_{10}$			336.2-338	169-70	0.793 (20°)
1,3-Diethylcyclohexane	$(C_2H_5)_2 \cdot C_6H_{10}$			336.2-339.8	169-71	0.796 (22°)
Cycloheptane	C_7H_{14}	10.4	-12	244.6	118.1	0.811 (20°)
Ethylcycloheptane	$C_2H_5 \cdot C_7H_{13}$	<-22	<-30	390.2	199	0.952 (20°)
Cyclooctane	C_8H_{16}	57.7	14.3	298.4-300.2	148-9	0.835 (20°)
Cyclononane	C_9H_{18}			341.6	172	0.773 (16°)

derivatives have been isolated, such as methylcyclopentane, methylcyclohexane, di- and trimethylcyclohexane.^{16, 64} No naphthenes with rings composed of more than six carbon atoms have been definitely identified in petroleum, and there is doubt of their existence in the oil because of insufficient stability. The gasoline naphthenes, therefore, consist of cyclopentane and cyclohexane and of their substitution compounds.

None of the individual naphthene hydrocarbons has been isolated from the higher-boiling products, such as kerosene and lubricants. However, Mabery and others early found this class of compounds up to $C_{26}H_{52}$ in Pennsylvania and Canadian petroleum. Table 3 shows some pertinent data developed by Mabery⁵⁰ on a viscous petroleum from Summerland, California, which he distilled under vacuum into fractions and then repeatedly redistilled and re-treated with concentrated sulfuric acid until the fractions boiled within a range of 9° F., and the oil no longer changed in gravity when further treated with sulfuric acid.

Table 3. Hydrocarbons of Summerland, California, Petroleum.

Hydrocarbon Series	Formula	Boiling Points at 60 mm. Pressure (°F.)	Specific Gravity at 68° F.
C_nH_{2n-2}	$C_{13}H_{24}$	150-155	0.8621
C_nH_{2n-2}	$C_{16}H_{30}$	175-180	0.8808
C_nH_{2n-4}	$C_{17}H_{30}$	190-195	0.8919
C_nH_{2n-4}	$C_{18}H_{32}$	210-215	0.8996
C_nH_{2n-6}	$C_{21}H_{44}$	250-255	0.9299
C_nH_{2n-8}	$C_{27}H_{46}$	310-315	0.9451
C_nH_{2n-8}	$C_{29}H_{50}$	340-345	0.9778

As indicated, the actual structure of these large saturated molecules poor in hydrogen has been the subject of much investigation and speculation, and the evidence is now almost conclusive that they are polycyclic and have one ring, or cycle, in the molecule for each pair of hydrogen atoms subtracted, the rings being joined through one, two, or more common carbon atoms, perhaps as in the partly or completely hydrogenated derivatives of anthracene, phenanthrene, retene, etc.

The most extensive investigation yet made of the lubricant fraction has been conducted in a unit of the American Petroleum Institute Research Project No. 6, by Rossini and his associates of the National Bureau of Standards, Washington, D. C.⁶⁵ A typical Mid-Continent petroleum, on which much other research had been done, was used for this purpose. Only a very brief abstract of the conclusions is permissible here. The unrefined lubricant fraction (a distillate), taken as 100 per cent, showed the following average analysis in reference to the kinds of molecules:

(1) About 43 to 51 per cent is composed of molecules having 1, 2, or 3 naphthene rings, together with the appropriate paraffin side chains.

(2) About 8.3 per cent is composed of molecules having 1, 2, or 3 naphthene rings and 1 aromatic ring, together with the appropriate paraffin side chains.

(3) About 8.1 per cent is composed of molecules having 2 naphthene rings and 2 aromatic rings (condensed) together with the appropriate paraffin side chains.

(4) About 6.6 per cent is composed of molecules having 1 naphthene ring and 3 aromatic rings (condensed) together with the appropriate paraffin side chains.

(5) About 18 to 26 per cent is composed of normal (straight-chain) paraffins, plus possibly some *isoparaffins* (branched-chain).

(6) About 8 per cent is composed of the "asphaltic" constituents, which have not been investigated.

The wax and asphaltic portions were isolated from this fraction, and the remainder, which was suitable for conversion into lubricating oil, had the composition: (1) about 60 per cent of naphthenes having from 1 to 3 rings per molecule (a very small proportion of material containing four naphthenic molecules was probably present also); (2) about 15 per cent of molecules having from 1 to 3 naphthenic rings and 1 aromatic ring per molecule, and with this substance was associated a small percentage of sulfur and oxygen compounds; (3) about 14 per cent of material having about 2 naphthenic rings and 2 aromatic rings (linked through 2 common carbon atoms) per molecule, and with this was associated a small proportion of sulfur and oxygen compounds; (4) about 11 per cent of material having 1 to 2 naphthenic rings together with more than 2 aromatic rings (probably linked through 2 carbon atoms) per molecule, and with this were associated some sulfur, nitrogen, and oxygen compounds.

All of the material contained molecules having one or more naphthenic rings, and thus there was no significant amount of purely paraffinic or aromatic hydrocarbons present.

The number of carbon atoms in the molecules of this fraction varied from about 20 for the lowest-boiling constituent to about 40 for the highest.

To illustrate their idea of a possible structure for a molecule containing two naphthene and two aromatic rings and having the empirical formula $C_{25}H_{34}$, these investigators assembled the following:

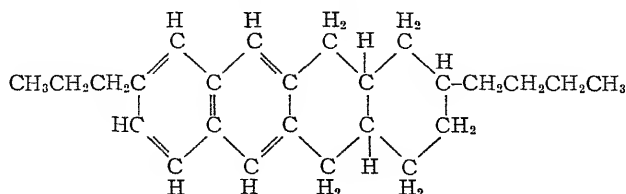


Table 4. Aromatic or Benzene Hydrocarbons.

Name	Formula	Melting Point (°F.) (°C.)	Boiling Point (°F.) at 760 mm. (°C.)	Sp. Gr. at °C.
Benzene	C_6H_6	41.9	176	0.878 (20°)
Toluene	$C_6H_5 \cdot CH_3$	-139.2	231.1	0.867 (20°)
Xylenes, dimethylbenzenes				
<i>o</i> -xylene	$C_6H_4 \cdot (CH_3)_2$	-16.6	291.2	0.879 (20°)
<i>m</i> -xylene	$C_6H_4 \cdot (CH_3)_2$	-53.3	282.6	0.864 (20°)
<i>p</i> -xylene	$C_6H_4 \cdot (CH_3)_2$	55.8	281.1	0.861 (20°)
Ethylbenzene	$C_6H_5 \cdot C_2H_5$	-137.2	277	0.867 (20°)
Trimethylbenzenes				
1,2,3-trimethylbenzene	$C_6H_3 \cdot (CH_3)_3$	-13.9	349.7	0.895 (20°)
1,2,4-trimethylbenzene	$C_6H_3 \cdot (CH_3)_3$	-49	336.6	0.876 (20°)
1,3,5-trimethylbenzene	$C_6H_3 \cdot (CH_3)_3$	-61.1	328.3	0.863 (20°)
Methylethylbenzenes				
1-methyl-2-ethylbenzene (<i>o</i> -ethyltoluene)	$C_6H_4 \cdot (CH_3) (C_2H_5)$		329	0.882 (20°)
1-methyl-3-ethylbenzene (<i>m</i> -ethyltoluene)	$C_6H_4 \cdot (CH_3) (C_2H_5)$		323.6	0.867 (20°)
1-methyl-4-ethylbenzene (<i>p</i> -ethyltoluene)	$C_6H_4 \cdot (CH_3) (C_2H_5)$	< -4	323.6	0.862 (20°)
<i>n</i> -Propylbenzene	$C_6H_5 \cdot C_3H_7$	-150.9	318.2	0.862 (20°)
Isopropylbenzene (cumene)	$C_6H_5 \cdot CH(CH_3)_2$	-142.4	307.4	0.862 (20°)
Tetramethylbenzenes				
1,2,3,4-tetramethylbenzene	$C_6H_2 \cdot (CH_3)_4$	24.8	399.2	0.901 (20°)
1,2,3,5-tetramethylbenzene	$C_6H_2 \cdot (CH_3)_4$	-11.2	384.8	0.896 (0°)
1,2,4,5-tetramethylbenzene	$C_6H_2 \cdot (CH_3)_4$	176	381.2	0.838 (81.3°)
Methylisopropylbenzenes				
1-methyl-2-isopropylbenzene	$C_6H_4 \cdot (CH_3) (C_3H_7)$	> -13	350.6	0.876 (20°)
1-methyl-3-isopropylbenzene	$C_6H_4 \cdot (CH_3) (C_3H_7)$	-100.3	347	0.860 (20°)
1-methyl-4-isopropylbenzene	$C_6H_4 \cdot (CH_3) (C_3H_7)$	-73.5	350.6	0.857 (20°)
Pentamethylbenzene	$C_6H \cdot (CH_3)_5$	127.4	446	0.853 (100°)
Hexamethylbenzene	$C_6 \cdot (CH_3)_6$	330.8	509	265
Pentaethylbenzene	$C_6H \cdot (C_2H_5)_5$	< -4	530.6	277
Hexaethylbenzene	$C_6 \cdot (C_2H_5)_6$	258.8	568.4	298

When fully hydrogenated, this substance would absorb 10 atoms of hydrogen per molecule and become $C_{25}H_{44}$. The hydrogenation in this molecule would occur at the 5 pairs of carbon atoms in the 2 aromatic rings joined by the double bonds, and the 2 aromatic rings would thus be changed into 2 naphthenic rings. The molecule would then contain 4 naphthenic rings.

Aromatic Hydrocarbons (C_nH_{2n-6})

Aromatic hydrocarbons of relatively low boiling points are found in certain petroleum, such as some of those of California and Borneo. They are also produced to some extent in certain oils in cracking operations at temperatures far too low for their formation through any known reactions, such as through acetylene. It is assumed that these aromatic hydrocarbons already existed in large complex molecules and were set free at the mild cracking temperatures. The aromatic hydrocarbons, benzene, toluene, dimethyl- and trimethylbenzenes, ethyl-, diethyl-, and triethylbenzenes, methylnaphthalene, etc., have been found in petroleum distillates. Table 4 contains some of the better known aromatic hydrocarbons, although they have not all been identified in petroleum.

The aromatic hydrocarbons react readily with concentrated sulfuric acid, a property which differentiates them fairly well from paraffins and naphthenes. They are also characterized by relatively high specific gravities.

Olefin (C_nH_{2n}) and Diolefin (C_nH_{2n-2}) Hydrocarbons

Olefins (Table 5) are differentiated from paraffin compounds by the presence of a double bond between some one pair of adjacent carbon atoms, as illustrated by the two isomers of butene: $CH_3 \cdot CH=CH \cdot CH_3$ and $CH_2=CH \cdot CH_2 \cdot CH_3$. As mentioned before, it is doubtful whether olefins occur in crude oil, but a high percentage is formed during cracking operations. They are much more reactive chemically than the paraffin and naphthene hydrocarbons.

Hydrocarbons of the non-cyclic type are known which contain two or more pairs of doubly linked carbon atoms. They are diolefins, triolefins, etc. One of the well known diolefins is isoprene, $CH_2=CH \cdot C(CH_3)=CH_2$, which is formed in the pyrolysis (cracking) of rubber or of turpentine. The diolefins as a class are chemically more active than olefins. With sulfuric acid they form tarry products. They are believed to be the principal cause of the instability of untreated cracked gasoline, producing "gums" and color. Table 6 shows a few of the important diolefins.

The olefinic hydrocarbons of low molecular weight, five carbon atoms or less, obtained by cracking petroleum and petroleum gases, constitute

Table 5. Olefin or Ethylene Hydrocarbons.

Name	Formula	Melting Point (°F.)	Melting Point (°C.)	B. P. at 760 mm. (°F.)	B. P. at 760 mm. (°C.)	Sp. Gr. at °C.
Ethylene	$\text{CH}_2=\text{CH}_2$	-272.9	-169.4	-154.8	-103.8	0.566 (-102°)
Propene	$\text{CH}_2=\text{CH}-\text{CH}_3$	-301.4	-185.2	-53.9	-47.7	0.610 (-47°)
Butenes						
1-Butene (ethylethylene)	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$	-202	-130	19.9	-6.7	0.617 (0°)
2-Butene (<i>cis</i> and <i>trans</i> mixture)	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$	-198.6	-127	32-37.4	0-3	0.628 (1.7°)
2-Methylpropene (isobutene)	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}_3$	-232.6	-140.7	20.1	-6.6	0.627 (-6.6°)
Pentenes						
1-Pentene	$\text{CH}_2=\text{CH}-(\text{CH}_2)_3-\text{CH}_3$			86.2	30.1	0.61 (20°)
2-Pentene (<i>cis</i> and <i>trans</i> mixture)	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$	-218.2	-139	97.5	36.4	0.61 (20°)
2-Methyl-1-butene	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}_2-\text{CH}_3$			87.8	31	0.61 (20°)
3-Methyl-1-butene	$\text{CH}_2=\text{CH}-\text{CH}(\text{CH}_3)-\text{CH}_3$	-211	-135	68.2	20.1	0.61 (15°)
2-Methyl-2-butene	$\text{CH}_3-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_3$	-191.2	-124	101.1	38.4	0.62 (20°)
1-Hexene	$\text{CH}_2=\text{CH}-(\text{CH}_2)_4-\text{CH}_3$			146.1	63.4	0.61 (20°)
1-Heptene	$\text{CH}_2=\text{CH}-(\text{CH}_2)_5-\text{CH}_3$			199.4	93	0.61 (20°)
1-Octene	$\text{CH}_2=\text{CH}-(\text{CH}_2)_6-\text{CH}_3$			253.4	123	0.61 (20°)
1-Nonene	$\text{CH}_2=\text{CH}-(\text{CH}_2)_7-\text{CH}_3$			294.8	146	0.61 (20°)
1-Decene	$\text{CH}_2=\text{CH}-(\text{CH}_2)_8-\text{CH}_3$			341.6	172	0.61 (20°)
1-Undecene	$\text{CH}_2=\text{CH}-(\text{CH}_2)_9-\text{CH}_3$			370.4	188	0.61 (20°)
1-Dodecene	$\text{CH}_2=\text{CH}-(\text{CH}_2)_{10}-\text{CH}_3$			415.4	213	0.62 (15°)
1-Tridecene	$\text{CH}_2=\text{CH}-(\text{CH}_2)_{11}-\text{CH}_3$			450.9	232.7	0.798 (20°)
1-Tetradecene	$\text{CH}_2=\text{CH}-(\text{CH}_2)_{12}-\text{CH}_3$			474.8	246	0.775 (20°)
1-Hexadecene (cetene)	$\text{CH}_2=\text{CH}-(\text{CH}_2)_{14}-\text{CH}_3$			525.2	274	0.784 (20°)
1-Octadecene	$\text{CH}_2=\text{CH}-(\text{CH}_2)_{16}-\text{CH}_3$			593.6	312	0.791 (20°)

Table 6. Diolefin Hydrocarbons.

Name	Formula	Melting Point (°F.)	Melting Point (°C.)	B. P. at 760 mm. (°F.)	B. P. at 760 mm. (°C.)	Sp. Gr. at 20° C.
Propadiene (allene)	$\text{CH}_2=\text{C}=\text{CH}_2$	-213	-136.1	-29.7	-34.3	0.610
1,3-Butadiene (erythrene)	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$			23	-5	0.680
1,3-Pentadiene (piperylene)	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$			109.4	43	0.681
2-Methyl-1,3-butadiene (isoprene)	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$	-232.2	-146.8	93.2	34	
2,3-Dimethyl-1,3-butadiene (diisopropenyl)	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{CH}_2$	-104.8	-76	156.4	69.1	0.726
1,5-Hexadiene (diallyl)	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$	-221.8	-141	140	60	0.688
2,4-Dimethyl-1,3-pentadiene	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2$			199.4	93	0.737
2,5-Dimethyl-1,5-hexadiene	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_2$			235.4	113	0.740
2,6-Dimethyl-1,5-heptadiene	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)-\text{CH}_3$			285.8	141	0.765

thus far the only important source of material from petroleum economically suitable for conversion directly into pure chemicals, such as the alcohols and ketones containing a corresponding number of carbon atoms. The vapor phase cracking methods give a high yield of these low molecular weight hydrocarbons. These olefinic gases are now converted on a large scale into valuable motor fuel of high antiknock characteristics by polymerization and by alkylation (combining of an olefin with an isoparaffin through the aid of a suitable catalyst).

Miscellaneous Hydrocarbons

Besides hydrocarbons belonging to the series already described, a large number of mixed types of compounds of carbon and hydrogen are found in petroleum. Such hydrocarbons may be composed either of straight chain or of cyclic compounds containing a variable number of rings, side chains, double bonds, etc., in a molecule. Their chemical formulas range from C_nH_{2n+2} to C_nH_{2n-20} ,⁵³ or possibly to molecules with even lower ratios of hydrogen to carbon, although the degree of hydrogen deficiency as shown by these molecular formulas may frequently be due not to double bonds but rather to ring structure.

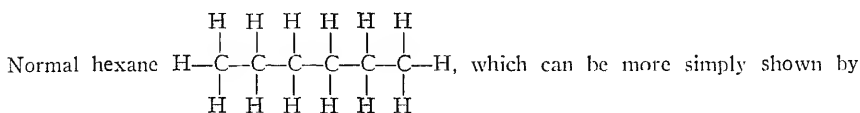
Mabery⁵⁴ considers the hydrocarbons of formulas C_nH_{2n-2} , C_nH_{2n-4} , especially C_nH_{2n-6} , and to some extent C_nH_{2n-10} and C_nH_{2n-18} to have the properties desired for lubricating oils. Davis and McAllister⁵⁵ believe that Pennsylvania lubricating oils contain essentially naphthene rings with paraffin chains, and they have proposed a formula which permits estimation of the number of carbon atoms in the naphthene nucleus from the molecular weight and density (see the more recent researches of Rossini and his associates, as noted above.⁵⁶) Zal'kind⁵⁷ thoroughly reviews the literature on the composition of petroleum, giving about 300 references, and comes to the conclusion that crude petroleum is characterized by a complete, or almost complete, absence of hydrocarbons having olefinic groups (double bonds).

Isomers

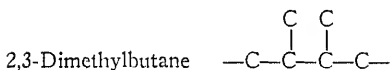
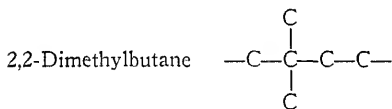
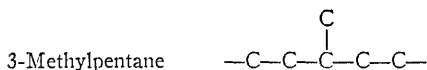
The initial two or three members of a homologous series of compounds, such as those found in petroleum, usually can exist in only one structural configuration; but in the succeeding members of the series, the number of structures or isomers increases rapidly. If any one carbon atom has a characteristic property that differentiates it from the other carbon atoms, for example, a double bond between it and another carbon atom or one bond attached to a distinctly different atom or radical, as a halogen, an —OH group, as in alcohols, or an —SH group, as in mercaptans, the number of configurations is further augmented. Since the isomers of the same molecule possess distinctly different boiling points and other different physical and chemical properties (note the hexanes and heptanes of Table 1, p. 16), it is obvious that data on the isomers of the larger but adjacent molecules would overlap and make more difficult, if not

impossible, the separation of one isomer from the others by any of the present known methods.

In Table 1 are shown the five isomers of the relatively small molecule hexane of empirical formula C_6H_{14} and consisting of 83.72 per cent carbon and 16.28 per cent hydrogen. The molecular structures of the isomers are:



omitting the hydrogen atoms, thus: $-C-C-C-C-C-C-$



The respective boiling points of these five isomers are: 68.7°, 60.2°, 63.2°, 49.7°, and 58.1° C.

Henze and Blair⁸⁸ and Perry⁶¹ have developed mathematical formulas for calculating the number of isomers in the paraffin and olefin hydrocarbons and in the alcohols, or any mono-substituted derivative of the paraffins. These chemists checked the accuracy of their formulas by writing all the possible structures of the alcohols up to and including the 12-carbon atom molecules, consisting of 3057 isomers, and of the paraffins through the 14-carbon atom molecules, consisting of 1858 isomers. Columns 2 and 3 of Table 7 enumerate these isomers. The olefin hydrocarbons of the last column show an even more rapid rise in the number of isomers with the succeeding molecules than the paraffins. Obviously not all these isomers are stable thermodynamically, and they cannot exist in petroleum. However, a sufficient number of them is present to make their separation from one another impossible except for the lowest members of the series. The quantities of the individual isomers are also small, as already noted.

The usual method for separating the lighter boiling-point constituents of petroleum is by distillation. By careful fractionation, which is now

Table 7. Possible Number of Isomers in Certain Organic Compounds.

Number of Carbon Atoms in Molecule	Mono-substituted Paraffins (Alcohols, Mercaptans, etc.)	Paraffin Hydrocarbons C_nH_{2n+2}	Olefin Hydrocarbons C_nH_{2n}
1	1	1	—
2	1	1	1
3	2	1	1
4	4	2	3
5	8	3	5
6	17	5	13
7	39	9	27
8	89	18	66
9	211	35	153
10	507	75	377
11	1,238	159	914
12	3,057	355	2,281
13	7,639	802	5,690
14	19,241	1,858	14,497
15	48,865	4,347	36,564
16	124,906	10,359	93,650
17	321,198	24,894	240,916
18	830,219	60,523	623,338
19	2,156,010	147,284	1,619,346
20	5,622,109	366,319	4,224,993
25	712,566,567	36,797,588	
30	95,991,365,288	4,111,846,763	
40		62,491,178,805,831	
60		22,158,734,535,770,411,074,184	

possible both with laboratory equipment, such as that developed by Podbielniak,⁶² and on a commercial scale, the lower members of the hydrocarbon series can be separated from one another. The Humble Oil Company, for instance, separates isopentane from other petroleum hydrocarbons in a practically pure state by employing a large number of plates in fractionating towers. However, difficulty in obtaining the desired separation increases for the higher-boiling fractions, which contain increasingly larger numbers of compounds boiling within very narrow temperature ranges. In the so-called true boiling point analysis, embodying the most efficient fractionation to which a hydrocarbon mixture can be subjected, the individual constituents are represented by plateaus on the boiling point curve. These plateaus disappear after the distillation curve reaches the region of hexanes or heptanes, and no more individual compounds can be distinguished in a graphical plot. Apparently the most feasible explanation of this behavior is that the heavier petroleum fractions consist of a large number of substances present in very small percentages and with boiling points very close together. This condition is also indicated by the results of the recent investigation of the composition of Mid-Continent crude petroleum, carried out under Project 6 of the American Petroleum Institute, which are summarized in Table 8.⁶⁴

The very small amount of any one higher molecular weight isomer or compound in petroleum and the inability to isolate one from another

Table 8. Hydrocarbons in a Mid-Continent Petroleum as Determined by American Petroleum Institute Research Project 6, National Bureau of Standards.

No.	Formula	Name and Type of Hydrocarbon	Boiling Point at 1 Atm. °C.	Purity of Best Sample Isolated (Mol Per Cent)	Estimated Relative Amount by Volume ^a
<i>Paraffinic</i>					
1	CH ₄	Methane	-161.7	b	b
2	C ₂ H ₆	Ethane	-88.6	b	b
3	C ₃ H ₈	Propane	-42.2	b	b
4	C ₄ H ₁₀	<i>Isobutane</i>	-12.1	b	b
5	C ₄ H ₁₀	<i>n</i> -Butane	-0.5	b	b
6	C ₅ H ₁₂	2-Methylbutane	27.9	b	b
7	C ₅ H ₁₂	<i>n</i> -Pentane	36.1	b	b
8	C ₆ H ₁₄	2,3-Dimethylbutane	58.0	>95	0.06
9	C ₆ H ₁₄	2-Methylpentane	60.3	>95	0.1
10	C ₆ H ₁₄	3-Methylpentane	63.3	>95	0.2
11	C ₆ H ₁₄	<i>n</i> -Hexane	68.7	98.3	0.7
12	C ₇ H ₁₆	2,2-Dimethylpentane	78.9	54	0.04
13	C ₇ H ₁₆	2-Methylhexane	90.0	99.9	0.3
14	C ₇ H ₁₆	3-Methylhexane	91.8	e	0.2
15	C ₇ H ₁₆	<i>n</i> -Heptane	98.4	>99.8	1.1
16	C ₈ H ₁₈	2-Methylheptane	117.2	97	0.5
17	C ₈ H ₁₈	<i>n</i> -Octane	125.6	99.1	1.0
18	C ₈ H ₂₀	2,6-Dimethylheptane	135.2	>99	0.1
19	C ₉ H ₂₀	<i>Isnonane</i>	140.8	85	0.05
20	C ₉ H ₂₀	4-Methyloctane	142.4	80	0.06
21	C ₉ H ₂₀	2-Methyloctane	143.3	99.9	0.2
22	C ₉ H ₂₀	3-Methyloctane	144.2	95	0.06
23	C ₉ H ₂₀	<i>n</i> -Nonane	150.7	99.9	1.0
24	C ₁₀ H ₂₂	<i>n</i> -Decane	174.0	>99.99	0.8
<i>Naphthenic</i>					
25	C ₅ H ₁₀	Cyclopentane	49.5	b	b
26	C ₆ H ₁₂	Methylcyclopentane	71.9	98.7	0.2
27	C ₆ H ₁₂	Cyclohexane	80.8	99.96	0.3
28	C ₇ H ₁₄	1,1-Dimethylcyclopentane	87.5	95	0.05
29	C ₇ H ₁₄	Methylcyclohexane	100.8	>99.8	0.3
30	C ₈ H ₁₆	Octanaphthene	119.8	b }	0.2
31	C ₈ H ₁₆	1,3-Dimethylcyclohexane	120.3	98 }	
32	C ₈ H ₁₆	Octanaphthene (1,2-dimethylcyclohexane?)	123.4	91	0.04
33	C ₈ H ₁₆	Ethylcyclohexane	131.8	95	0.1
34	C ₉ H ₁₈	Nonanaphthene (alkyl cyclopentane)	136.7	>99	0.1
35	C ₉ H ₁₈	Nonanaphthene	141.2	95	0.08
<i>Aromatic</i>					
36	C ₆ H ₆	Benzene	80.1	99.8	0.08
37	C ₇ H ₈	Toluene	110.6	b	0.3
38	C ₈ H ₁₀	Ethylbenzene	136.2	95	0.03
39	C ₈ H ₁₀	<i>p</i> -Xylene	138.4	>99.9	0.04
40	C ₈ H ₁₀	<i>m</i> -Xylene	139.2	>99.9	0.1
41	C ₈ H ₁₀	<i>o</i> -Xylene	144.4	>99	0.1
42	C ₉ H ₁₂	<i>Isopropylbenzene</i>	152.4	98.4	0.03
43	C ₉ H ₁₂	1,3,5-Trimethylbenzene (<i>mesitylene</i>)	164.6	99.95	0.02
44	C ₉ H ₁₂	1,2,4-Trimethylbenzene (<i>pseudocumene</i>)	169.2	99.9	0.2
45	C ₉ H ₁₂	1,2,3-Trimethylbenzene (<i>hemimellitene</i>)	176.1	99.95	0.06

^a The numbers in this column give the estimated relative amounts by volume of the given hydrocarbon in the petroleum, referred to normal octane or normal nonane (which are present in substantially equal amounts) as unity. In order to obtain the order of magnitude of the *percentage content* of the given hydrocarbon in the original crude, these figures should be multiplied by a factor which is roughly estimated to be somewhere between 1 and 1.66

^b Not determined.

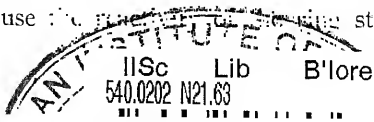
^c Determination not yet completed.

will doubtless to a considerable extent prevent an extensive conversion of petroleum hydrocarbons into pure organic chemicals heretofore known, although some success has already been attained in the manufacture of fatty acids. The low molecular weight hydrocarbons, particularly the low molecular weight olefins, which result from the cracking operations, constitute an abundant supply of raw material for chemicals, as noted elsewhere. On the whole, it seems certain that the total amount of chemicals other than motor fuels to be manufactured from petroleum will for a long time constitute only a minor portion of the total volume of petroleum products sold. The present achievements in manufacturing chemicals from petroleum are summarized in the fundamental treatises of Ellis.³¹ Figure 1⁴ gives an example of chemicals which can be derived from pentane. Brooks¹⁵ has pointed out some aspects of the future developments of chemicals from petroleum.

Analysis of Petroleum Hydrocarbons

The tremendous amount of work done on the chemical composition of petroleum has generally been conducted along two rather independent lines: isolation of various compounds present in petroleum; and synthesis of different types of hydrocarbons followed by a study of their characteristics in comparison with those of the individual petroleum fractions. The former encounters the difficulty of separating the individual compounds without changing their structure, whereas the latter encounters the difficulty of attempting to synthesize an infinite number of substances, only a very few of which may actually be found in nature.

Investigations which have been made on the separation of various petroleum constituents are well summarized by Gurwitsch.³⁷ Within the last few years, further researches along similar lines have been stimulated by the development of new chemico-physical methods, such as the studies of Raman spectra,² specific dispersions,⁷⁴ refractive indices,⁴⁸ fractional solubilities in solvents,⁵⁸ fractional diffusion,³ specific refractions,⁷³ crystal structures,⁴⁶ infrared absorption spectra,⁴⁷ the depressing of boiling points on mixing the hydrocarbons with substances such as aniline,³⁵ optical activity,³⁴ and other methods. The earlier methods of separating the members of individual series from one another and from members of other series by distillation, sulfonation, nitration, chlorination, bromination, etc., have been largely supplemented by hydrogenation, solvent extraction, and other new developments. Attempts have been made to analyze hydrocarbon mixtures in terms of the characteristic radicals rather than by separating and isolating the individual components. This appears to be of considerable interest, because the structure is



540.0202

greatly dependent on the length and number of side chains if the number of carbon atoms in the side chains is above a certain minimum.⁷³

Of the recent researches conducted on synthesizing hydrocarbons with specific reference to petroleum problems, those of Hugel,⁷⁴ Mikeska,⁷⁵ Mair and Willingham,⁷⁴ and Müller and Pilat⁷⁷ deserve particular attention.

A series of simplified laboratory methods has been developed for analyzing petroleum products and for correlation purposes. They permit a rough estimation of the composition of petroleum distillates in terms of the most important classes of hydrocarbons. However, because of variations in chemical activity and other properties of the individual members of each series, such methods are at best only approximations.

Egloff and Morrell⁷⁵ calculate the antidetonating properties of gasolines from their chemical composition. Morrell and Levine,⁷⁶ Sachanen,⁷⁶ Kurtz and Headington,⁴² Thomas, Bloch, and Hoekstra,⁷² Fisher and Eisner,⁷³ Steinbrecher and Kühne,⁷⁰ and others have devised a number of similar methods for estimating approximate percentages of the hydrocarbons of different homologous series present in light petroleum distillates. A very interesting work similar in scope has been under way for several years by Watson, Nelson, and Murphy.⁷⁰ This work has resulted in the development of the "characterization factor" for petroleum oils, which is believed to be related to their chemical composition, although it might be calculated on the basis of simple laboratory tests. This characterization factor has been correlated to a number of properties of petroleum oils which are of importance for both engineering and chemical purposes.

It is of interest that hydrocarbons of acetylene or terpene series have never been found in uncracked petroleum oils, although they may be present in small quantities in cracked products.

As the main constituents of petroleum oils are hydrocarbons, and as hydrocarbons are generally believed to be colorless, some have assumed that the color of the oil depends entirely on the nature and quantity of the so-called impurities present. On the other hand, theories, perhaps poorly founded, have been advanced that "white oils" do not exist as such in the original crude oil but are formed as a result of chemical changes during the acid or chemical treatment.⁴⁴ A recent synthesis of a blue-colored hydrocarbon is, therefore, of interest in connection with the foregoing speculations.⁷

Oxygenated Compounds

Oxygenated compounds found in petroleum or its products may be present in the crude oil, or they may be formed in the distillation or in contacting oils with atmospheric oxygen. In crude petroleum the quantity of oxygen seldom exceeds 0.5 per cent, although in exceptional cases it may be as high as, or higher than, 7.0 per cent.

In general, petroleum or its products may contain various types of acids, aldehydes, alcohols, or phenols, as well as compounds of as yet

undetermined chemical structure. Acids are the most important of these constituents of the oil, and as a rule, they are naphthenic or polynaphthenic in type. Only small quantities of fatty acids are present in crude oil, such as formic, acetic, isoamyl-acetic, diethylpropionic, or other low-boiling members of the series. However, some crude oils contain some high molecular weight fatty acids, such as palmitic, stearic, myristic, and arachidic.

Naphthenic acids, by far the most important oxygenated compounds found in the crude petroleum, are frequently isolated from the oil during refining operations and used for manufacturing by-products, such as soaps, for home or industrial uses. Oils containing these acids are corrosive to distillation equipment and may have undesirable characteristics after they are refined unless the acids are completely removed. Crude oils rich in naphthenic acids are usually of naphthenic type, such as those of the Gulf Coast or of California.¹⁰

Phenols (phenol, cresols, xylenols)⁷⁸ may be present in cracked distillates from which they are sometimes isolated and sold. Aldehydes are also found in cracked distillates and are believed to be responsible for much of the gum formation.⁶⁹ Alcohols, ketones, and other oxygenated compounds occur in oils oxidized at relatively high temperatures.

The oxygenated compounds in petroleum oils are usually eliminated in the course of refining. They are easily attacked by sulfuric acid, solvents, clay, and particularly by solutions of alkali. In exceptional cases, however, their removal presents a serious difficulty and may require certain changes in the scheme of refining.

Although the oxygenated compounds are usually considered undesirable in the oil, some of them are known to improve its resistance to atmospheric oxidation (autoxidation). For example, some cracked gasolines become less stable by washing with caustic soda solution. However, other cracked gasolines may become more stable when washed with the caustic solution because of the removal of certain oxygenated compounds that act as accelerators of the oxidation reactions.

Nitrogen Compounds

Practically all petroleum contains combined nitrogen, although usually in a small quantity, 0.1 per cent or less. Certain crude oils are found, however, which have a nitrogen content of one per cent or more; and inasmuch as a single nitrogen atom may occur in a large molecule composed otherwise of only hydrogen and carbon, it is possible that the nitrogen compounds may run as high as 10 or 20 per cent of the oil.

Little is known about the constitution of these substances as found in crude oil, since they undergo chemical modification during distillation.

The decomposition products may be of aromatic or hydroaromatic type, or may bear a very close resemblance to alkaloids, as found in an extensive investigation by Bailey and his associates.⁸ Many of these substances are of the quinoline or pyridine type and are easily extracted from the oil by sulfuric acid as the sulfate salts, or by solvents. However, an appreciable percentage of the nitrogen compounds is not basic in character, and therefore is not completely removed by the above chemicals.

Most of the nitrogen compounds apparently have no deleterious effect on the finished products and therefore need not be removed. However, some of them, especially in cracked distillates, possess an unpleasant odor¹³ and a reddish color.¹⁸ The usual nitrogen compounds of the laboratory, when placed in motor fuels, have different effects on the detonating qualities of the fuels; some of them suppress detonation (primary and secondary amines), some of them increase it (propyl nitrate), and some are practically neutral (pyridine)¹¹; but as yet the influence of those naturally occurring in the oil has not been determined. Obviously the presence of nitrogen compounds detracts somewhat from the heating values of fuels, but this effect is of little commercial significance because of the low percentage of the nitrogen. A good review of the present knowledge of nitrogen compounds in petroleum is given by Ellis.³¹

Sulfur Compounds

All petroleum contains sulfur, which may vary in quantity from a few tenths or hundredths of one per cent in Pennsylvania, Mid-Continent, or Peruvian crude oils to seven or eight per cent in certain crude oils from Mesopotamia. Of the American oils, the richest in sulfur are those in certain oil fields of California, Ohio, Canada, and Mexico, where the oil may contain as much as three to four per cent sulfur. In general, the sulfur content seldom exceeds one per cent. As sulfur compounds are objectionable in most of the finished petroleum products, their elimination is one of the problems in the refining of oils having a high sulfur content.

Elemental sulfur and a few types of combined sulfur have been identified in petroleum and its products. The compounds found are hydrogen sulfide, carbon disulfide, mercaptans, or thioalcohols, thioethers, thiophenes, thiophanes, organic disulfides and polysulfides, and organic sulfates. Some of these compounds are undoubtedly present in the crude petroleum; some (mercaptans) are formed during cracking; and some (sulfates, disulfides) are formed in chemical refining. The most important of these compounds will be discussed in more detail in connection with the various refining operations. Unfortunately the constitution of the greater percentage of the sulfur compounds associated with petroleum and its products, particularly those which are the most difficult to remove, is as yet

unknown, and as a result the desulfurization methods now employed are mainly of an empirical nature.*

Sulfur compounds are commonly considered objectionable in finished oils because of their actual or potential corrosiveness, disagreeable odor, deleterious effect on color or color stability, and unfavorable influence on antiknock and oxidation characteristics. In refining oils, sulfur compounds may be removed or changed into other sulfur compounds which are considered less harmful. In refined fuel oils, such as gasoline, the sulfur compounds may be objectionable not only because of their immediate corrosiveness to metals but also because of the corrosiveness of the sulfur dioxide produced in combustion. Immediately corrosive to metals are hydrogen sulfide, sulfur dioxide in the presence of moisture, relatively large percentages of elemental sulfur (0.15 gram per liter or more) in oil free of mercaptans, or very slight traces of elemental sulfur (0.01 gram per liter) in oil containing mercaptans. Mercaptans themselves in oil are not corrosive unless elemental sulfur is also present.

Inasmuch as all the sulfur, whether elemental or combined, is converted into sulfur dioxide during combustion in an engine, an investigation was made by Diggs²² to determine the maximum amount of sulfur permissible in gasoline without causing serious corrosion due to the tendency of the sulfur dioxide to collect in the lubricant, where it combines with traces of moisture to form sulfurous acid, which attacks the bearing surfaces. He found in the motor as manufactured at that time that a sample of gasoline containing 0.46 per cent sulfur produced very corrosive conditions, one with 0.15 per cent a slight but appreciable corrosion, whereas one with 0.04 per cent sulfur was harmless. This research, and others, indicated that about a 0.10 per cent maximum limit of the sulfur content of gasoline, as was required in the governmental specifications, was a safe allowance. Other investigations were in agreement with these conclusions, as gasoline with 0.16 per cent sulfur was considered corrosive, whereas 0.11 per cent sulfur had relatively little effect on the equipment, and 0.06 per cent sulfur was without action.⁶³ It is certain, however, that in cars equipped with ventilators for the crankcase and thermostatic controls for the radiators, corrosion can be reduced to negligible proportions by preventing any collection of water and sulfur dioxide in the crankcase. Because of the effect of temperature, there is now little or no danger of corrosion from sulfur dioxide in warm weather;²⁷ and as the removal of sulfur from the oil is in many cases very expensive, especially from the cracked distillates, suggestions have been made that the problem be solved

* A very complete bibliography of the literature and patent references on the chemistry of sulfur as related to the petroleum industry has been compiled by Borgstrom, Bost, and Brown.¹²

either by using suitable non-corrosive alloys in constructing certain parts of the motor or by varying the maximum allowable sulfur content in the gasoline with the season of the year, but neither idea seems practical. It should be pointed out that gasolines sold in certain parts of Europe contain more than 0.50 per cent sulfur and apparently have no bad effect on engines. In countries with a rather uniformly warm climate, like California, the use of gasolines of high sulfur content is quite general. The government specifications are gradually being extended to accept 0.25 per cent sulfur. (*Also see page 223.*)

Sulfur in gasoline does not materially affect the knock rating of the gasoline itself, but it does very seriously decrease the efficiency of tetraethyl lead if the latter is added to gasoline to increase the octane rating of the gasoline. It lowers the lead "susceptibility."

In other petroleum products sulfur is also deleterious. The quality of lamp oils is impaired by a large percentage of sulfur. Kerosenes with a high sulfur content burn in a lamp with a reddish fringe, smoke the chimney, and deposit on the chimney a white film, which gradually darkens. Investigations have shown that one volume per cent of sulfur compounds and of halogen compounds in kerosene increases the soot-forming property of the kerosene by ten and seven times, respectively.⁷⁵

In lubricating oils, sulfur compounds may not be objectionable. Kalichevsky⁴⁰ has discussed the use of various addition agents to motor and similar lubricating oils. Some of these agents contain sulfur, and it is possible that at least some of the crude oils may contain sulfur in a form that is beneficial to the functioning of lubricating oils made therefrom. Considerable investigational work is needed, however, before definite appraisal of the sulfur compounds in lubricating oils can be made, but it now appears doubtful whether the opinion of some refiners is justified that a high sulfur content in lubricating oils is indicative of inferior quality of the oil.

Mineral Constituents

The amount of mineral constituents in crude oil usually varies from a few hundredths to a few tenths of one per cent. In addition to the elements already mentioned, there may be sodium, potassium, lithium, calcium, strontium, barium, iron, aluminum, copper, silver, phosphorus, arsenic, vanadium, manganese, and even silicon, tin, lead, cobalt, titanium, gold, chromium, nickel, argon, and helium.⁴⁹ The metals are usually in combination with naphthenic acid as soaps, although phosphides or sulfides of arsenic have also been isolated. As stated before, some of the inorganic constituents occur only in the water emulsified in the oil.

Crude oils containing large proportions of inorganic constituents are

frequently treated for the removal of the latter, as these substances tend to accumulate in the residuum during distillation and to affect its properties unfavorably. The methods of desalting the crude oils are in some respects akin to those employed in breaking crude oil emulsions; namely, after the oil is emulsified with enough additional water to dissolve the salts, the emulsified water is then separated from the oil by electrical, centrifugal, or other means commonly in use for handling water-in-oil emulsions.³⁰

Some of the mineral constituents are unavoidably introduced into the oil during refining. Thus sodium or calcium salts of sulfonic acids may be left in small amounts in the oil after refining the oil with sulfuric acid and neutralizing with sodium hydroxide or lime.

In general the mineral constituents should be removed so as to prevent them from producing ash when the oil is burned. Ash deposits in engines result in abrasion of the moving parts of the engines, and the ash from heavy fuel oils is injurious to the brick walls of furnaces.

Although mineral constituents in petroleum products are generally undesirable, small percentages of such materials are frequently added to oils to improve their performance. Thus tetraethyl lead is employed to raise the octane rating of gasoline, and various agents containing metals are added to lubricating oils to improve their lubrication.

PRINCIPAL COMMERCIAL PRODUCTS FROM PETROLEUM

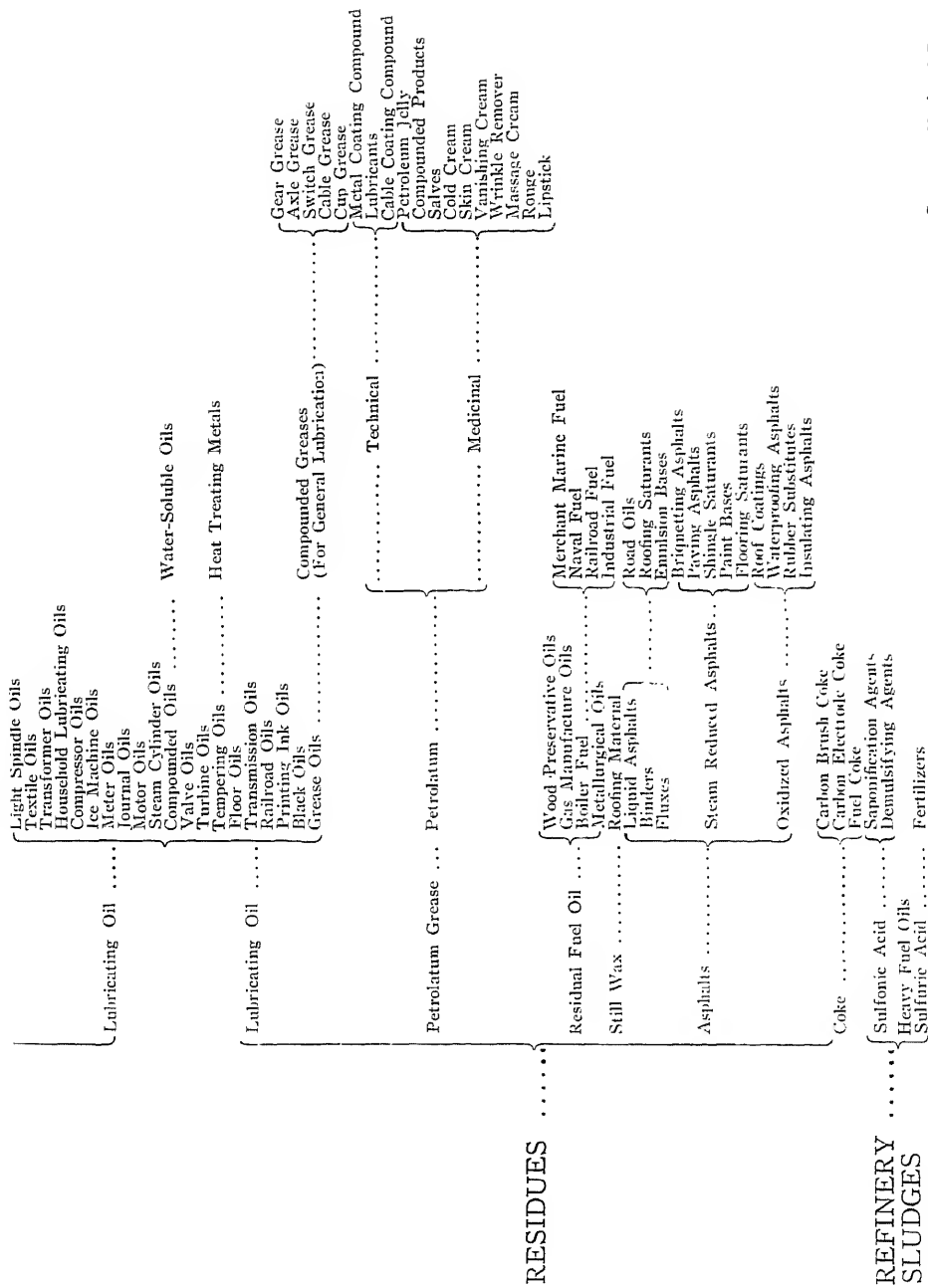
A large variety of products is now made from petroleum. Both the general procedure of refining the crude oil and to some extent the choice of the crude oil used are determined by the type of product to be manufactured. Some of the important products from petroleum are shown in Fig. 2.⁵ Each of these products may be refined in a variety of ways. The kerosene fraction, for example, may be converted into tractor fuel, Diesel engine fuels, lamp oil, incubator oil, or heating oil, all of which are different in their physical and chemical properties.

When the crude oil is received at the refinery, it may first be subjected to desalting operations or it may be washed with caustic soda for the removal of naphthenic acids, hydrogen sulfide, etc.; but the first major treatment is the distillation. Although the distillation procedures vary with the individual refineries, two general types are recognized. In one, no effort is made to prevent thermal decomposition, or cracking, of the heavier fractions; in the other, extreme care is exercised to prevent such decomposition. In the first procedure, the distillation is usually conducted at high temperatures with no steam or only a very small quantity of steam to aid the process; in the second procedure, the distillation is conducted at

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<p>Liquefied Gases { Illumination Gas { Laboratory Ether { Petroleum Ether { Motor Priming Ether</p> <p>Alcohols { Isopropyl { Secondary Butyl { Secondary Amyl { Secondary Hexyl</p> <p>Other Synthetics { Benzene { Toluene { Nylene { Naphthalene { Anthracene { Resins { Rubber Tires { Inks { Paints</p> <p>Gas Black { Fuel Gas { Light Naphthas</p>	<p>HYDROCARBON GASES</p>
<p>Naphthas { Intermediate Naphthas { Heavy Naphthas</p> <p>Refined Oils { Kerosene { Signal Oil { Mineral Seal Oil { Carburition Oils { Metallurgical Fuels { Cracking Stock { Household Heating Fuels { Light Industrial Fuels { Diesel Fuel Oils { Gasoline Recovery Oil { Benzol Recovery Oil { White Oils</p> <p>Gas Oil { Absorber Oil</p> <p>Technical Heavy Oil { Saturating Oils { Emulsifying Oils { Electrical Oils { Flotation Oils { Candymakers Wax { Candle Wax { Laundry Wax { Sealing Wax { Etchers Wax { Saturating Wax { Chewing Gum Wax { Medicinal Wax { Insulation Wax</p> <p>Wax { Cardboard Wax { Match Wax { Paper Wax</p>	<p>LIGHT DISTILLATES</p>
<p>Gasoline { Lamp Fuel { Stove Fuel { Motor Fuel { Railroad Signal Oil { Lighthouse Oil { Coach & Ship Illuminants { Gas Absorption Oils</p> <p>Technical { Emulsified Spray Oils { Bakers Machinery Oil { Candymakers Oil { Fruit Packers Oil { Egg Packers Oil { Slab Oil—Candy and Baking { Internal Lubricant { Salves { Creams { Ointments</p> <p>Medicinal { Wool Oils { Twine Oils { Cutting Oils { Transformer Oils { Switch Oils { Metal Recovery Oils</p> <p>Detergent Wax { Iron Wax</p>	<p>INTERMEDIATE DISTILLATES</p>
<p>Gasoline { Gas Machine Gasoline { Petroleum { Hexane { Chemical Solvents { Aviation Gasoline { Motor Gasoline { Commercial Solvents { Blending Naphthas { Varnishmakers & Painters Naphthas { Dyers & Cleaners Naphthas { Turpentine Substitutes { Soaps</p> <p>Technical { Rubber Solvent { Fatty Oil Solvent (Extraction) { Lacquer Diluents</p> <p>Medicinal { Domestic Illumination Naphtha { Candlepower Standardization Naphtha { Laboratory Naphtha { Drug Extraction Solvent</p>	<p>HEAVY DISTILLATES</p>

HEAVY
DISTILLATES



Courtesy, National Petroleum News.

FIGURE 2. Important Products Derived from Crude Petroleum.

relatively low temperatures but with the aid of a large quantity of steam, preferably under reduced pressure. The first procedure is used when it is not desired to manufacture lubricating oils, for it is usually believed that the desirable properties of lubricating oil stocks are injured or partly destroyed by high temperatures, and the yield of oil of a given viscosity greatly reduced. However, no definite information is available regarding the stability of lubricating oils prepared from cracked residues; and, at least in some instances, it appears possible to convert such cracked residues into lubricating oils possessing very satisfactory characteristics.

Bell ⁹ describes in detail the present refinery distillation equipment, and Sachanen ⁴⁷ discusses the chemistry and technology of cracking. Nelson ⁶⁰ discusses the design of distillation and cracking equipment as applied to petroleum problems.

The main products that result from the distillation of all crude oils are gasoline, kerosene, gas oil, lubricating oil, and, when asphalt-base crude oils are distilled, a residuum suitable for the manufacture of asphalt.

Gasoline

Gasoline consists of a mixture of aliphatic, olefinic, aromatic, and naphthenic hydrocarbons boiling within a certain temperature range, which varies within the specification limits for the individual products. These specifications vary with the grade of gasoline and depend on whether it is to be used in automobile motors, in aviation motors, etc. The initial boiling point of gasoline is usually preferred to be in the neighborhood of 70 to 90° F., and is adjusted to fit the needs of the individual engines and the season of the year. The end, or highest, boiling point of the gasoline varies from 300° F., or less for aviation fuels, to 437° F. (225° C.), or even higher for the heavier grades of motor fuels. The end boiling point of 400° F. is now most commonly accepted for the better grades of motor gasoline.

Commercial gasoline is in reality a blend of a number of substances, the most important of which are as follows: natural, or casinghead, gasoline obtained by liquefying the vapors of the higher boiling point hydrocarbons occurring in natural gas either by compressing the gas (compression gasoline, method now obsolete), by absorbing the vapors in an absorbent oil (absorption gasoline), or by adsorbing with charcoal and other solid adsorbents (adsorption gasoline, a process with little commercial application); a product sometimes referred to as conservation gasoline, which is similar to the above, but is obtained by applying any of the above processes to the light hydrocarbon vapors evolved from refinery stills or storage tanks; cracked gasoline obtained from heavy crude oil fractions, usually gas oils, by cracking them in the liquid phase (liquid-phase cracked gasoline) or vapor phase (vapor-phase cracked gasoline), the first product

being somewhat easier to treat than the second, but possessing poorer anti-knock characteristics; reformed gasoline, obtained by cracking fractions of petroleum which boil practically within the boiling point range of gasoline, so as to improve the antiknock or the volatility properties; polymerization gasoline, made by polymerizing the olefins of cracked hydrocarbon vapors, or by simultaneously cracking and polymerizing the normally gaseous petroleum hydrocarbons found in refinery or natural gas; alkylation gasoline, obtained by combining an isoparaffin with an olefin with the aid of a catalyzing agent, such as 98 per cent sulfuric acid; and hydrogenated gasoline, obtained by hydrogenation of cracked or polymerized gasolines containing a large percentage of unsaturated compounds, hydrogenation and cracking being frequently performed in a single operation. Obviously not all refineries have all these products at their disposal, but they should have available a sufficient variety to enable them to prepare a gasoline that will meet market specifications. Blending is important, because a gasoline from a single operation as a rule cannot meet commercial specifications, for such a gasoline is either too volatile (natural gasoline, conservation gasoline, or certain types of polymerization gasoline), or has an unsatisfactory boiling point distribution curve (certain types of straight-run or cracked gasolines), or does not meet specific requirements, such as anti-knock rating, saturation, etc.

The different gasolines are refined by various methods, the choice of method depending on properties of the raw material and the refining agents available. The raw materials are usually treated more economically before they are blended into the commercial gasoline. Some of the materials suitable for gasoline manufacture are used in the manufacture of other products, such as cleaners' naphtha (approximate boiling range, 200°-300° F.), cleaners,' or Stoddard, solvent (boiling range, 300°-400° F.), rubber solvents, lacquer and paint thinners, etc., each of which requires different methods of refining.

In some European countries, constituents derived from sources other than petroleum, such as alcohols, benzene, etc., may be blended with the petroleum gasoline to make motor fuels.* The possibility of using alcohol in motor fuels in America has received some attention, but it is not economical for the consumer. Although some justification can be found for employing alcohol as motor fuel in countries poor in natural resources and surrounded with enemies that could exclude the importation of petroleum products, such a situation does not exist in the United States where petroleum resources are bountiful, and the addition of alcohol to gasoline

* Nash and Howes²⁰ give a comprehensive discussion of the various blends of alcohols with particular reference to England. The greater expense of such blends to the consumer has been extensively discussed in the literature.²⁰

would introduce an inferior quality fuel at a cost to the consumer greater than that of gasoline. The argument in favor of blending with alcohol in the United States is at present decidedly unsound economically. It would subsidize the agricultural industry at the expense of the consuming public. Such subsidizing would appear to be especially unwarranted when it is considered that actually the alcohol (ethyl, or grain) is being produced on a large scale from petroleum much more cheaply than it can be produced from grain.

Kerosene

Kerosene is employed primarily for illuminating and heating purposes. Its average boiling point is above that of gasoline, and the boiling range of its constituents runs from an initial boiling point of 300-350° F. up to a final boiling point of 500-600° F. Kerosene intended for illuminating purposes must pass rigid tests for burning quality, as described in subsequent chapters. These burning qualities are unfavorably affected by aromatic hydrocarbons, which are therefore eliminated by drastic refining.

Certain petroleum fractions boiling within the kerosene range are utilized as commercial solvents. In contrast to a good kerosene, such solvents should contain aromatic hydrocarbons for their solubility characteristics. For this reason, these solvents are frequently made most economically from the aromatic material extracted from the kerosene stock in the course of refining the kerosene.

As mentioned above, many other commercial products are prepared from the fraction of oil having the kerosene boiling range, such as fuel for Diesel motors, absorbent for natural gasoline, etc., but in general the demand for all these products has not kept pace with the amount of kerosene stock produced. Much of the stock is, therefore, converted by cracking operations into lower-boiling hydrocarbons suitable for gasoline.

Gas Oil

Gas oil is a rather indefinite term usually applied to petroleum fractions having viscosity and boiling point ranges intermediate between those of kerosene and lubricating oils. Its characteristics vary and depend on the more or less complete utilization of the lighter and heavier petroleum fractions in the course of manufacture. Gas oil is now for the most part converted into gasoline, although appreciable quantities of it are employed as domestic or commercial fuels and for the manufacture of artificial gas (hence its name). It is also used as fuel for certain types of Diesel engines, especially high-speed engines. Contrary to the non-detonating property sought in gasoline, Diesel fuel must possess poor antiknock characteristics, or a high cetene (or cetane) number. With the progress in the design of

Diesel engines, the requirements for Diesel fuels gradually become more severe, and it seems reasonable to assume that in time the specifications for Diesel fuels will be as rigid as they are at present for gasoline.

Gas oil may contain both straight-run and cracked products, such as recycle stock. As a rule, no special attempt is made in the refineries to segregate the individual components of gas oil if it is to be used for cracking purposes; but at times it is economical to crack the straight-run and the recycle stock separately because the optimum cracking conditions for the two are not the same.

Lubricating Oils

Lubricating oil is also a rather indefinite term. Lubricating oils comprise not only those fractions of petroleum which are employed for lubricating machinery but also oils which are used for entirely different purposes, such as transformer or cable oils. Lubricating oil stock is usually considered to include all the distillate obtainable from the crude oil after the gas oil has been expelled, as well as some of the residues that are left in the still when non-asphaltic crude oils are distilled. These residues cannot be distilled economically. They are also referred to as cylinder stocks or steam cylinder stock; the latter names were originally derived from the use of the stock for oiling steam cylinders, but now the terms are used with little discrimination for all types of residual stocks, including those which are employed in the manufacture of motor or airplane engine oils.

The residuum left from distilling asphalt-base crude oils is generally used for the manufacture of asphalt or for fuel oil. The lubricating oil is made almost exclusively from the distillates, although in some cases it is possible to make lubricating oil from the residuum by the proper use of solvent refining. The lubricating oil stocks as obtained from the stills may be refined with chemicals, and may either be used directly as lubricating oils or be blended with other distillate or residual stocks from paraffin-base crude oil to meet required specifications. For instance, it is common practice to prepare a distillate stock and a residual stock and then blend these two components in the desired proportions to yield lubricating oils of intermediate viscosities. It is also possible to prepare similar finished lubricating oils directly from a paraffin-base residuum which still contains a considerable portion of distillable materials. When the latter method is employed, *i.e.*, when the viscosity of the residual stock is relatively low, the residuum is frequently termed "long residuum."

The lubricating oils are made into thousands of products which may consist of the pure mineral oils or blends containing one or more other ingredients, such as those derived from vegetable, animal, or mineral sub-

stances. These added ingredients may vary in quantity from a few tenths of one per cent to 50 per cent or more. Among these products are motor oils, aviation oils, Diesel oils, machine oils, transformer oils, switch oils, turbine oils, cable oils, perfumery oils, medicinal oils, insecticidal oils, cutting oils, "soluble" oils, leather oils, textile oils, loom oils, etc.

Lubricating oils blended with large quantities of vegetable or animal oils are commonly known as compounded oils. Lubricating oils which are rendered semi-solid or solid by addition of soaps or similar materials are classified as greases.⁴¹

Asphalt

The term "asphalt" in the petroleum industry applies to the semi-solid or solid residuum left in the stills after the volatile fractions from an asphalt-bearing crude oil are removed. If, however, the distillation is carried still further so as to decompose or crack the asphalt as well as to distill all of the volatile fractions, the residue is known as coke.

Asphalt may be used as it is obtained from the stills, but it is commonly subjected to additional treatment, such as oxidation with air, sulfurization, partial distillation for removing traces of the oil, etc. Many asphaltic products are made and are used for paving, for impregnating roofing paper, etc. A complete discussion of the asphalt and asphaltic products is beyond the scope of this book, and the reader is referred to other treatises on this subject, particularly to that of Abraham.¹

The separation of crude oil into the several arbitrary fractions by no means makes them marketable as finished products. The fractions must be refined to eliminate the deleterious and chemically unstable constituents and to add desirable properties which experience and rigid specifications demand.

Although the succeeding chapters discuss further the chemistry of petroleum, they are intended to deal more specifically with the use of chemicals and reagents in the purification of oils and improvement in the qualities of the oils. For references on the chemistry and properties of petroleum, the reader should consult such treatises as those of Bacon and Hamor,⁶ Brooks,¹⁴ Engler-Höfer,³² Gruse,³⁶ Gurwitsch,³⁷ Sachanen,⁶⁶ Redwood,⁶³ Ellis,³¹ Egloff,²⁵ Dunstan, Nash, Brooks, and Tizard,²⁴ and others. For information on refinery installations, equipment, processes of distillation, etc., the reader is referred to the works of Bell,⁹ Campbell,¹⁷ Cross,¹⁹ Day,²¹ Leslie,⁴⁵ Nelson,⁶⁰ and others.

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Chapter II

Treatment with Sulfuric Acid

As pointed out in Chapter I, the first step in refining petroleum is the distillation operation for separating the oil into its various fractions. These fractions must be further refined with chemicals to eliminate certain constituents that have an unfavorable effect on the finished oils. It should be noted that, with few exceptions, distillation is the cheapest refining process; for this reason it is used as much as possible in the purification of the different products.

Chemical refining is effected by such reagents as sulfuric acid, caustic alkalis, alkaline plumbite solution, organic solvents, fuller's earth, and a number of other substances which have special selectivity in the removal of undesirable constituents. This refining eliminates the more unstable hydrocarbons, the resinous and asphaltic substances, some of the oxygen, sulfur, and nitrogen compounds, and in some instances certain classes of the hydrocarbons themselves, such as the aromatics from kerosene.

The sequence in the application of reagents to an oil is important and usually follows a fixed routine; for instance, after treatment with acid an oil is neutralized with alkalis or adsorbents. Sometimes it may be desirable to treat the oil with alkalis both before and after the acid refining. Adsorbents are usually applied as the final operation rather than as the first operation. They should be used to remove only the impurities that the cheaper acid cannot remove. These general observations on chemical refining are made here for illustrative purposes, and they will be discussed in more detail in connection with each individual reagent.

Among the chemical refining agents, sulfuric acid has long had the most general application. It was first employed for refining animal and vegetable oils, and since the beginning of the petroleum industry, about ninety years ago, sulfuric acid has been successfully applied to the purification of practically all petroleum products.

According to Rather, sulfuric acid was applied to "coal oils" by Tower in England in 1792.¹⁹⁸ As early as 1770, Bridges⁹⁸ refined spermaceti by boiling it with dilute sulfuric acid; and in 1792, Gower¹⁰¹ refined animal oils with dilute sulfuric acid. These methods appear to be the first on record in which sulfuric acid was used in the refining of oily materials.

A number of patents for the use of sulfuric acid were issued at the very beginning of the petroleum industry. Thus Young²⁰⁸ and Atwood and Atwood⁹ treated oil distillates with sulfuric acid and alkalis; Merrick¹³⁰ treated the still bottoms from the

redistillation of petroleum distillates with sulfuric acid; Burges¹³² treated naphtha with sulfuric acid and alkalies, mixed it with potassium cyanide, sodium borate, and salts of tartar, and used the naphtha for extracting grease in the tanning industry; Kendall¹³³ treated oil distillate with acid, etc.

Because of its cheapness, the possibility of minimizing its severity of action by choice of concentration and temperature, and its almost universal applicability to the many refining problems, sulfuric acid has been for many years by far the most important reagent for treating oils. More recently, however, its importance for certain types of oils has declined considerably because of the development of solvent refining processes, which are described in Chapter VII. Nevertheless, solvents are not always satisfactory substitutes for sulfuric acid; and, moreover, they can be cheaply applied to the oils only when treating on a very large scale. For this reason it appears certain that sulfuric acid will continue to be of considerable importance in refining for many years to come.

The action of sulfuric acid on petroleum is complex, and the whole behavior is only partly understood. Strong acid attacks or can be made to attack almost all the constituents of the oil, including saturated hydrocarbons and resinous and asphaltic substances, as well as compounds containing sulfur, nitrogen, and oxygen. The selective action of the acid on these compounds can be increased, often to a marked degree, by varying the conditions of treatment, such as temperature, concentration of the acid, time of contact, etc. The action of the acid on petroleum products is generally both chemical and physical (solvent), but the differentiation between the two is usually difficult and often, but not always, of minor importance in refinery practice.

Action of Sulfuric Acid on Paraffins

The chemical action of sulfuric acid on paraffins has been the subject of many investigations, and the results obtained by different investigators are not always in agreement. The information on this subject is discussed and to some extent summarized below.

Methane is the only paraffin which is entirely unattacked at normal temperatures by either concentrated or fuming acid.⁷⁸ Ethane, propane, and butane are very slowly attacked by fuming sulfuric acid containing 12 per cent or more of sulfur trioxide²⁴² or by acid of approximately the same concentration as that required for the sulfonation of the liquid members of the paraffin series.³³ Orndorff and Young¹⁸⁴ report that 50 per cent of a sample of propane was absorbed on standing 15 days over oleum. Worstall²⁶⁰ found that by dropping oleum into pure boiling hexane, heptane, or octane, about 30 to 40 per cent of each was converted into mono-sulfonic acids, and the remainder completely oxidized. These hydrocarbons

react at a very slow rate, however, in the cold. Istrati and Mihailescu¹²⁴ report that warm concentrated sulfuric acid acts upon hydrocarbons or paraffins having high melting points. Burkhardt³⁷ found that when an excess of hexane, cyclohexane, or methylcyclohexane is vigorously agitated for four to five hours at 32 to 50° F. with fuming sulfuric acid, containing 35 to 65 per cent free sulfur trioxide, practically all the sulfuric anhydride enters into the reaction, and the sulfonation reactions are extensive. About one molecule of sulfur dioxide is produced from the acid per molecule of hydrocarbon. At high temperatures the percentage of hydrocarbons oxidized is greater. It is also known that the "acid sludge" produced from these reactions when left for a considerable length of time yields much sulfur dioxide, a by-product of the oxidizing action of the sulfuric acid on the organic matter of the sludge.

At elevated temperatures all hydrocarbons, without exception, are oxidized by sulfuric acid, and consequently many of the reports of the literature appear somewhat conflicting unless the temperature, strength of the acid, time of contact, and purity of the chemicals are considered. Some investigators report that at normal temperatures acid of 85 per cent concentration has a slow chemical action on paraffins and that acid of 90 per cent⁴⁰ or 93 per cent concentration¹⁴⁹ has an appreciable action. Other investigators set the limit of concentration of the acid at about 98 per cent and observe a decided sulfonating effect of acid of 100 per cent strength or higher.¹⁸²

The solubility of paraffin hydrocarbons in sulfuric acid increases with increasing strength of the acid; and, with the possible exception of the gaseous hydrocarbons, the solubility also increases with the molecular weight of the hydrocarbons.^{108, 261} The structure, or space configuration, of the molecule greatly influences the behavior of the molecule with acid; the more complex molecules, especially those having a hydrogen atom attached to a carbon atom which in turn is attached to three other carbon atoms, are more easily attacked by the acid than the molecules with a simpler structure.^{33, 25} The complex molecules oxidize more readily and have much less tendency to knock when used as fuel in an automobile engine.

In usual refinery practice, it seems improbable that paraffins, especially those possessing the normal structure, are appreciably sulfonated, although they may be dissolved to some extent in the acid sludge.¹⁰⁸

Saturated aliphatic and cyclic hydrocarbons are capable of reacting with aliphatic aldehydes and ketones in the presence of sulfuric acid. Commercial utilization of these reactions has been suggested, for example, in condensing petroleum ether with acetone, etc.¹⁸⁰ Such findings serve to disprove the generally accepted theories that the paraffin hydrocarbons are inert toward most chemical reagents.

Because of the comparative insolubility and chemical inertness of nearly all the paraffin hydrocarbons in sulfuric acid under ordinary conditions of refining, acid treatment tends to increase the relative proportion of the paraffins in the refined product in comparison with the original stock by eliminating the non-paraffin hydrocarbons. Many of the trends of the last few years have shown that, contrary to previous conceptions, paraffin compounds are in some cases the least desirable constituents of the refined product and that, with a few exceptions, drastic refining of certain petroleum oils should be avoided. In motor fuels paraffin hydrocarbons as a class are conducive to detonation; in lubricating oils they are decidedly inferior to the usual hydrocarbons which form the body of the oil.³³

However, this statement does not apply to all the paraffins, as some of them may possess very valuable properties which make them desirable as constituents in motor fuels. Thus, 2,4,4-trimethyl pentane (commercial isoöctane) possesses high antidetonating properties⁶⁹ and is used in aviation fuels and as an antiknock reference standard. These findings show that generalizations covering a certain class of hydrocarbons must be made with caution, for any one class may contain a few subclasses or individual compounds which behave differently from the other members.

Action of Sulfuric Acid on Naphthenes

Naphthenes (C_nH_{2n}) are very similar to paraffins in their behavior toward sulfuric acid, and under ordinary refining conditions are not appreciably attacked by concentrated or by fuming acid, although when associated with other hydrocarbons they may also be dissolved to some extent by sulfuric acid. Their resistance to sulfuric acid is, however, somewhat less than that of paraffins; and some of the lower members of the series react slowly with ordinary concentrated acid. Thus cyclopropane and 1,1-dimethyl-cyclopropane under favorable conditions are attacked by concentrated sulfuric acid,¹⁵⁴ whereas an acid containing 10 per cent of sulfur trioxide also attacks higher members of the series, such as 1,4-dimethyl-2-ethylcyclopentane, and the like.²⁶⁵

The effect of the acid on naphthenes is much more intense at higher temperatures.¹⁰⁸ It has been shown that the naphthene hydrocarbons which boil between 250 and 500° F. can be sulfonated by acid of 96 per cent concentration.^{80, 221} In addition to sulfonation, some oxidation and resinification always occur. Dehydrogenation may also take place.¹⁵⁸ The acid sludge from their treatment is, therefore, complex and, as to be expected, of a dark color.^{154, 155, 79}

Menshutkin and Wolf²⁰⁸ show that, on treating cyclohexane with fuming sulfuric acid, benzene derivatives are produced in small amounts. Such dehydrogenation reactions seem to explain to a certain extent the tendency of naphthenes and paraffins to enter into condensation reactions by replacing a hydrogen with a hydrocarbon group.

Naphthenes as a class are more desirable constituents in motor fuels than paraffins since they possess superior non-detonating properties, although, as in the paraffins, variations in the individual members exist.⁷² Inasmuch as naphthenes of the same boiling point as paraffins have higher specific gravities, it is obvious that the low specific gravity limitations for gasolines formerly required militate against the best fuel, and such specifications are being entirely eliminated from the oil industry. Morrell and Egloff¹⁷² enumerate various methods of estimating the different types of hydrocarbons in gasoline.

Action of Sulfuric Acid on Aromatics

Aromatic hydrocarbons are considerably more reactive with sulfuric acid than either paraffins or most of the naphthenes, although they are sufficiently resistant toward it to require certain modifications in the usual refinery practice when their complete removal is desired. The reactivity of the individual members of the series varies considerably; whereas benzene, *p*-di-substituted benzenes, and tetra-substituted benzenes are not readily attacked at ordinary temperature by an acid weaker than 95 per cent, toluene and other homologs are sulfonated by acid of 91 to 92 per cent concentration.²³⁷ It has been shown that an acid of 85 per cent concentration may remove about 30 per cent, and an acid of 88 per cent concentration about 50 per cent of toluene from its mixture with cracked spirits.^{72, 229} For these reasons, none of the many proposed tests for the determination of aromatics in the presence of olefins by means of sulfuric acid is reliable, though a few of them may serve roughly some particular purpose for which they are intended.

Howes¹¹⁸ shows that sulfuric acid cannot be used for separating olefins from gasoline quantitatively since the acid also attacks the aromatics. Other reagents are also unsatisfactory: bromine and iodine form substitution products but can be used for certain purposes when approximate data only are required; mercury salts either oxidize olefins or form addition compounds and, moreover, fail to react with some of the olefins; ozone, thiocyanates, aluminum chloride, hydrogen peroxide, liquid nitric oxide, and potassium permanganate are also non-selective; and sulfur monochloride attacks paraffins. There is no reagent available which shows accurately the quantity of olefins in the presence of aromatics, and the use of sulfuric acid for an approximate estimation is justified only because of the simplicity of the method. Vlughter²¹⁰ hydrogenates the olefins before applying sulfuric acid to the blend to remove the aromatics.

In refinery practice, 93 per cent acid (66° Bé.) is the weakest that can be used economically for the removal of relatively large percentages of aromatics, and its action is, as a rule, far from complete. Fuming acid is used in preference to weaker acid in producing high quality lamp oils, in which oil the aromatics are objectionable because they burn with a smoky flame. Treating the kerosene stock at relatively high temperature

may be advisable, since sulfonation of aromatics proceeds much faster, and the acid is more efficiently utilized.⁹⁰ However, temperatures in excess of 120 to 130° F. are seldom used in refining lamp oils for reasons to be explained later.

Action of Sulfuric Acid on Unsaturated Hydrocarbons

Unsaturated hydrocarbons, olefins, diolefins, acetylenes, etc., are, as a rule, readily attacked by sulfuric acid of even as low as 75 per cent concentration and at ordinary temperature. The reactivity varies, however, for different groups and for the different members of the same series to such an extent that some of them may require a very drastic acid treatment for their removal. These variations in reactivity can sometimes be utilized for analytical purposes. Thus a mixture of ethylene, propene, isobutene, and erythrene, usually found in the gases involved in the pyrogenetic decomposition of petroleum, can be analyzed on the basis of their selective solubility in sulfuric acid of different concentrations.⁶³

Olefins are produced in large quantities in cracked distillates and to some extent in overheated distillates. In the refining of motor spirits, the constituents completely soluble in sulfuric acid at ordinary temperatures often consist of a high percentage of the lower members of the olefin series.²⁵⁷ They are considerably more reactive than the higher members.

Olefins, with the exception of those that react at normal temperatures with free oxygen, are desirable constituents in gasoline because of their high octane values, and their conservation in refining is important. For these reasons, opinions have been expressed that the specifications for gasolines concerning their odor, color, and color stability in light should be omitted, as these specifications have no, or very little, relationship to the desirable characteristics of the finished product but may necessitate the use of large quantities of chemicals in refining, with the consequent removal of some of the olefins.

At the beginning of the present trend in the use of high compression ratios in motors, it was advocated that a test be introduced which would require a certain percentage of unsaturated hydrocarbons, or equivalents, in the standard gasoline.²⁰ However, a much more logical procedure is the present method of specifying antiknock values. Likewise, a milder refining of lubricating oils than now practiced is often permissible, as some of the constituents removed by the acid are in part responsible for the viscosity of the oil. These constituents of lubricants are not olefinic, as often assumed in the past.

Engloff and Morell⁷² earlier considered that the presence of one volume of unsaturated hydrocarbons in gasoline has approximately the same antidetonating effect as 0.2 volume per cent of aromatics, although in the light of more recent investigations

no such quantitative relationships can be established because of the wide variations in the antidetonating properties of individual hydrocarbons belonging to the same class of compounds. In general, the loss in antiknock rating with acid treatment depends on several factors, notably on the nature and source of the gasoline,²⁵⁵ and it cannot be estimated without actual experimentation. In the laboratory, care should be exercised to prevent the loss of volatile constituents which contain high octane values. Their loss may otherwise be incorrectly attributed to the effect of the acid.

Recently a series of tests has been introduced by the United States Government and some other countries which serve to eliminate olefins from aviation gasolines. These tests include the acid heat values and the bromine index. The acid heat value is expressed as the temperature rises in degrees Fahrenheit observed on mixing gasoline with sulfuric acid under the experimental conditions. The bromine index is supposed to measure total unsaturation, etc. The value of these tests is doubtful, and they seem particularly useless because the specifications further require the gasoline to pass a number of rigid oxidation tests which are sufficiently severe to insure storage stability. It appears that previous experiences with motor gasolines have been largely overlooked by those responsible for the tests, and it seems desirable that these tests should be abandoned.

When olefins are treated with sulfuric acid, some polymerization to dipolymers and higher polymers takes place, as well as formation of secondary and tertiary alcohols and of the acid and neutral esters of the sulfuric acid. No tars are formed by treatment of any pure olefin with strong sulfuric acid at 60° F. The reaction products are mainly removed from the oil as part of the acid sludge, but some of them, such as the polymers, higher alcohols, alkyl sulfates, and apparently certain other compounds, the character of which is not well known, but which contain sulfur introduced into the hydrocarbon molecules by the acid itself, remain dissolved in the distillate. On redistillation, the alkyl sulfates break down into alcohols, unstable hydrocarbons, sulfur dioxide, etc., and cause trouble from gums, loss of color, corrosion, etc. The esters are not removed by caustic washing, as they are insoluble in alkalis; but they decompose when heated above 285° F.^{33, 247} The quantity of these sulfuric esters found in the refined product is roughly inversely proportional to the amounts of sulfuric acid used.²⁰ An excess of acid produces the acid sulfuric esters, which are largely removed by caustic washing. Moreover, the alkyl sulfates and acid alkyl sulfates are extracted by sulfuric acid when a large amount of the latter is used.

The relative importance of the miscellaneous reactions which occur between the olefins and sulfuric acid varies widely and depends primarily upon their constitution and molecular weight. The chemical reactivity of the olefins with sulfuric acid increases with the molecular weight to a maximum with the pentenes and hexenes; above these it decreases. The tendency to polymerization then becomes much more marked and is still distinctly pronounced even with dodecene, $C_{12}H_{24}$. For example, Brooks and Humphrey^{33, 183} found that dodecene gave the polymer $C_{24}H_{48}$ almost quantitatively. However, this latter polymer, which still

contains a double bond linkage, is very stable to sulfuric acid and does not polymerize further under normal refining conditions. The higher polymers are not removed by the acid, even by acid of 100 per cent concentration,⁸¹ and because their viscosity is higher than that of the corresponding saturated hydrocarbons,^{33, 183} they are suitable constituents for lubricating oils.

Many suggestions have been made that light oils could be treated with sulfuric acid, aluminum chloride, or similar polymerizing agents,¹⁶¹ and the polymers recovered and used for manufacturing various higher-boiling products.²⁰⁵ The more concentrated sulfuric acid favors polymerization reactions. These reactions proceed very rapidly with an acid of 100 per cent strength. Long time of contact also favors the formation of polymers and not of alcohols.^{33, 183} If the oil is heated during acid treatment, it yields polymers which have different properties from those obtained by treating at normal temperatures.

Polymerization of the lower members of the olefin series is now an important refinery process, and it results in a higher total yield of gasoline from the original crude oil. The raw materials are either the unsaturated hydrocarbon gases formed in the cracking operations or the saturated hydrocarbon gases containing two or more carbon atoms in a molecule and which are first converted into unsaturated hydrocarbons by thermal decomposition at high temperatures.

The polymerization can be effected with or without the use of catalysts. The basic non-catalytic processes now in commercial use are known as the "Unitary Thermal Process"⁵⁰ and the "Multiple Coil Thermal Process."⁵ The former operates at a temperature of 960-1100° F. and at a pressure of 1000-3000 pounds per square inch; the latter operates at 900-1300° F. and at pressures up to 800 pounds per square inch. In the Multiple Coil Thermal Process, the unsaturated compounds are polymerized at 900-1000° F. and 600-800 pounds pressure, the non-condensed portions being reprocessed for production of additional quantities of unsaturated hydrocarbons at 1150-1300° F. and 50-75 pounds pressure and then fed to the raw charge.

The best known catalytic processes are those employing sulfuric acid,^{51, 147} phosphoric acid,⁷⁰ and a catalyst prepared by the Catalytic Development Company.¹¹⁷ Polymerization is effected by passing the gases containing the unsaturated hydrocarbons through a catalyst bed or through the sulfuric acid solution under proper temperature conditions and sometimes under moderate pressure. The catalytic processes now in use are not yet suited for simultaneously decomposing the saturated hydrocarbons into olefins and polymerizing the latter, and for this reason such catalytic processes are best applied to gases which contain large proportions of the unsaturates.

The polymerized gasolines have a high antiknock rating and consequently are valuable blending agents for motor fuels. The refinery unsaturated gases may be fractionated so as to yield mainly the butene fraction. This fraction, kept in the liquid state under pressure, is thoroughly washed with sodium hydroxide solution or other reagents to remove all traces of hydrogen sulfide or other sulfur derivatives that would interfere with the life of the catalyst in subsequent processing. The purified hydrocarbons are then passed through the catalyst, and the unsaturates are polymerized into dipolymers, or commercial isoöctene. To a certain extent other butenes than the isobutene are polymerized without unduly affecting the isoöctane rating of the final product. Isobutene is the easiest to polymerize, but it is economical to include a certain amount of the other butenes. Certain quantities of the undesirable trimers and higher polymers are also formed, but they are kept at a minimum by

proper control of the polymerization conditions. The dipolymer, or the isoöctene, is hydrogenated to yield commercial isoöctane by one of the known hydrogenation processes. The olefins are readily hydrogenated, and the high pressures can, therefore, be avoided by using the mild hydrogenation processes developed for this particular purpose.²¹⁴ The hydrogenation operation is rather expensive and can be carried out only by large plants, as large quantities of hydrogen must be produced. It is often desirable to produce the polymers at the various refineries and then ship them to a central point for hydrogenation.

The unblended isoöctane obtained as described above is not suitable for use in aviation motors because of insufficient volatility. It is, therefore, blended with a light gasoline fraction, usually isopentane, which can be prepared in an amply pure state by the modern fractionation methods. Tetraethyl lead is then added to the resulting blend to raise its octane number to the desired level.

Closely related to the manufacture of high octane fuel from the conversion of low molecular weight olefins to gasoline by polymerization is the alkylation process now in general use in refineries that have cracking units. In this alkylation process, isoparaffins, especially isobutane, are made to combine with an olefin, *e.g.*, butene, through the agency of a catalyst, such as sulfuric acid.¹⁸ This combination of the olefin and isoparaffin yields the saturated hydrocarbon isoöctane.

Inasmuch as the low molecular weight olefins can be converted by polymerization or alkylation into the valuable motor fuels, semi-commercial developments have already been made in preparing the olefins themselves by catalytic dehydrogenation of the gaseous paraffins, ethane, propane, butane, etc.¹⁶⁵ It is reported that, whereas the yield of *n*-butene from *n*-butane by the older thermal process is not greater than 15 per cent under the most favorable conditions, the yield by catalytic dehydrogenation is 85 to 95 per cent. The catalysts used are the oxides of such metals as chromium, molybdenum, vanadium, titanium, and cerium, supported on carriers of low catalytic activity, such as aluminum and magnesium oxides.

Further discussion of polymerization is omitted as the subject pertains to the manufacture of chemicals from petroleum rather than to refining. The use of petroleum as raw material for the synthesis of chemicals is discussed by others.^{67, 70}

Alcohols are formed from olefinic hydrocarbons in contact with acid at low temperatures. The so-called hydrated esters^{33, 183} of sulfuric acid on treatment with water form secondary and tertiary alcohols. The formation of alcohols from olefins under the action of sulfuric acid has been known for at least 65 or 70 years;⁸⁷ but the reaction was utilized commercially only a relatively few years ago¹³⁶ when large volumes of olefins became available from cracking operations.

Brooks³¹ has discussed the commercial synthesis of the different alcohols and related products from petroleum. Reactions of commercial interest for manufacturing alcohols from hydrocarbons have been described in a number of articles which refer to production of amyl alcohols from pentane,¹⁹⁰ isopropyl alcohol from propene by absorption in 97 per cent sulfuric acid,¹¹⁴ secondary and tertiary alcohols from lighter hydrocarbons from vapor phase cracking,⁶⁷ ethyl alcohol from ethylene,⁶⁰ alcoholates and other products from cracked kerosene through reaction with sulfuric acid at 32 °F.,⁸⁵ etc.

In preparing isopropyl alcohol from propene, the latter, occurring in cracked refinery gases, is passed through sulfuric acid solution under carefully controlled conditions so as to obtain the maximum yield of alcohol and the minimum of polymers. Acid of about 87 per cent strength is

suitable, and the process is best conducted a little below 85° F.^{76, 148} and under ample agitation to prevent undesirable local reactions. After the proper period of contact, the sulfuric acid and its absorbed material are settled from the main volume of hydrocarbons, mixed with water for hydrolysis of the esters, and subjected to distillation to remove the alcohols.

The acid sludge obtained from treating olefinic hydrocarbons, *i.e.*, cracked oils, with sulfuric acid may be used for the production of substances other than alcohols, *e.g.*, the direct electrolytic oxidation of the potential alcohols in the sludge to ketones.⁷⁷ Processes covering these reactions are numerous; but as they do not strictly concern chemical refining of oils, their further description is omitted, and readers are referred to other books on these subjects.^{75, 67}

With an excess of strong sulfuric acid, *i.e.*, about 98 per cent strength, some saturated hydrocarbons are formed from both olefins and alcohols, and some higher molecular weight unsaturated hydrocarbons are likewise formed and are dissolved by the acid.²⁶

Olefins in general do not affect the color and odor of a treated oil. Diolefins are objectionable and are usually considered to be the tar-forming substances and to be partly the cause of the discoloration and resinification, or gumming, of gasolines in storage. Isoprene and dimethylbutadiene are good examples of diolefins that show such behavior. The removal of diolefins is, therefore, considered one of the main purposes of the acid refining of cracked oils. Some of their polymerization products may, however, possess valuable lubricating properties, and their exclusion from the refined lubricating oils may not be desirable.⁶⁸ Because of the chemical reactivity of diolefins their separation from other hydrocarbons is not particularly difficult.

Gasolines refined with substances other than sulfuric acid so as to leave the percentage of olefins undiminished have remained water-white in color and have kept a sweet odor for two years, and in both respects were better than the corresponding samples refined with acid.^{23, 153}

In the treatment of petroleum products with sulfuric acid, some of the acid is almost always reduced to sulfur dioxide. This sulfur dioxide may also react with some of the unsaturated hydrocarbons, forming various addition products and thus complicating still further the nature of the basic reactions. Reactions between sulfur dioxide and olefins have been investigated.¹⁵⁷ It has been found that the reaction products may be of the type of sulfones or polysulfones, or they may be of heteropolymeric type that have properties of plastics. These types of reactions may explain the anomalous behavior of some of the cracked distillates which, when treated with progressively larger quantities of acid, first show a decrease

in the sulfur content, then a marked increase, and then with still larger amounts of acid a decrease in the sulfur content. Examples of such behavior will be given later in this chapter.

This short discussion of the reactions which occur between sulfuric acid and the unsaturated hydrocarbons indicates that any extensive removal of the latter, especially from motor fuels, is not desired. Only the more reactive compounds need be removed.

The compounds requiring partial or complete elimination from petroleum products are the resinous and asphaltic substances, the oxygenated or partially oxidized substances, the nitrogen compounds, and the sulfur compounds, all of which are discussed below.

Resinous and Asphaltic Substances

Little is known of the chemical constitution of resinous and asphaltic substances. It is usually assumed that traces of such compounds are responsible for the color in petroleum distillates, and their elimination is sought. The action of sulfuric acid on these compounds is thought to proceed in accordance with the general equation of adsorption:¹⁰⁸

$$C' = kC''^n$$

where

C' = Concentration of asphalt in the oil,

C'' = Concentration of asphalt in the acid,

k and n = Constants.

Sulfuric acid easily removes resinous and asphaltic substances from petroleum. About three to five pounds of concentrated sulfuric acid per barrel is reported as being sufficient in most instances for the removal of the resinous constituents of petroleum oils which hinder crystallization of wax in wax-bearing lubricating distillates.⁴⁷ As resinous substances inhibit crystallization of wax, their removal from oil often results in a rise in its "pour point" after sulfuric acid treatment, since the wax then has an opportunity to crystallize and destroy the fluidity of the oil.

The influence of resins in inhibiting wax crystallization has been discussed by Kalichevsky.¹²⁰ When Grozny crude oils are treated with fuming sulfuric acid in the preparation of medicinal oils, the pour point of the oil rises, but the coefficient of refraction, specific gravity, viscosity, and aniline point decrease.²³⁰ However, not all resins act as inhibitors in the crystallization of wax.²⁴⁴

The action of concentrated sulfuric acid on asphalt varies according to the nature of the asphalt. Soft asphalt is dissolved by sulfuric acid. Hard asphalt is irreversibly flocculated or coagulated by concentrated sulfuric acid, and this physical change is usually accompanied by simultaneous chemical reactions, especially those of oxidation (more sulfur dioxide is liberated from sulfuric acid by hard asphalt than by soft asphalt.¹¹⁰)

Patents exist for the use of relatively dilute sulfuric acid for the removal of insoluble or unstable carbonaceous material or sediment of unknown chemical composition from the heavy residuum produced in cracking operations. Some of these residual oils, which are suitable only for fuels, possess the property of forming more sediment, even after the oil is once made free from it by filtration or by other methods. Small quantities of dilute acid (*e.g.*, 0.5 per cent of 40 per cent acid) are used for treating these residues to coagulate the sediment, since stronger acid would form a large volume of sludge.⁹⁰ A short period of heating to about 150° F. with weak acid is claimed by one inventor to be beneficial.¹⁷⁶ Such treatment may also be applied to the cracked distillate fuels which otherwise may be unstable in storage. As a rule however the loss to sludge is always very great, and the process makes the cost almost, if not completely, prohibitive. The tendency is to sell such residual fuel to consumers who can keep it mixed or agitated until it is burned.

Oxygenated Compounds

A great variety in kind and quantity of oxygenated compounds occurs in crude oils and their distillates, as discussed in Chapter I. Oils contain only a small percentage of these substances, and in ordinary refinery practice their removal from the oil by means of acid is usually incomplete (possibly not over 50 per cent is removed). However, in a pure state (not diluted with oil) naphthenic acids and phenol-like substances are dissolved by acid. Some of them are sulfonated, some oxidized,¹⁹⁷ and some are first oxidized and then dissolved in the acid.

It has been observed that, in the refining of kerosene, sulfuric acid does not act chemically on naphthenic acids but does react with phenols.²²⁸ The application of sulfuric acid to oil bearing naphthenic acids and the recovery of the latter have been described in the patent literature.²⁵²

Phenols are not, however, subject to the action of cold concentrated sulfuric acid any more than are aromatic hydrocarbons,²²⁶ with the exception of the homologs of high molecular weight or very complex structure. It is possible that phenols form condensation products with certain naphthenes during the acid treatment.²⁰⁶ They may also form colored condensation products with olefinic hydrocarbons.²³¹

Oxygenated compounds should generally be avoided in refined oils, as some of them possess undesirable acidic properties, and others are the gum-forming substances.³³

Oxygenated compounds may be of value in petroleum oils used for lubricating purposes. They may improve the oiliness of the oil, as discussed in greater detail in Chapter XI. For this reason recommendations have been made that some of the

petroleum acids be left in lubricating oils. For motor oils the optimum proportion is below two per cent.²¹⁰ However, the value of such products for general lubricating purposes is controversial.

Nitrogen Compounds

As pointed out in the preceding chapter, nitrogen compounds of basic nature are easily removed from the oil even by weak sulfuric acid. The non-basic nitrogen compounds are considerably more resistant to sulfuric acid treatment.

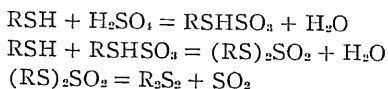
Nitrogen bases can be isolated from petroleum by treating with an acid which does not form sludge, *e.g.*, with dilute sulfuric acid of not over 50 per cent strength, and then neutralizing the acid with sodium carbonate to free the nitrogen bases.¹⁷⁴ Countercurrent washing of gasolines¹²² or of the extracts from liquid sulfur dioxide treatment¹²¹ with an acid of about 25 per cent strength is practical, particularly when a high percentage of nitrogen bases is present. The use of weak acid for the recovery of nitrogen bases obviously must precede refining with strong acid¹⁷⁷ if the latter is required for treating the oil. The recovered nitrogen bases can be fractionated by making use of their differential solubilities in water.^{121, 122} Nitrogen bases extracted from petroleum products are used to some extent as insecticides and wood preservatives.

Sulfur Compounds

A brief discussion of sulfur compounds in petroleum products was presented in the preceding chapter. It has been shown that not all of them are harmful in refined oils, and that a few may even be beneficial.

The action of a large amount of sulfuric acid on the extraction of a few of the sulfur compounds common to petroleum distillates has been investigated, and the results are here summarized.

Mercaptans are oxidized to disulfides, and the acid reduced to sulfurous acid:



A small quantity of elemental sulfur is also formed from a side reaction, caused by a reduction of the sulfuric acid.¹⁵ The final products, the disulfides, are partly removed in the sulfuric acid sludge. The "sweetened" gasoline may turn sour again by reduction or by decomposition of the disulfides to mercaptans. The completeness of the removal of mercaptans from the oil is greatly dependent on the strength and amount of the acid; fuming acid is the most active, 93 per cent acid is considerably less active, and 73 per cent acid is almost without action.²⁵⁸ As a large amount of

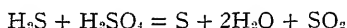
acid is necessary to remove all the mercaptans, complete sweetening of gasoline is never attempted in this manner.

Alkyl disulfides are soluble in acid of strength greater than 93 per cent but are only slightly soluble in acid of 73 per cent strength. Their solubility in the acid is less, however, than that of alkyl sulfides. They are converted to mercaptans by reducing agents, as noted above.^{257, 258} Discoloration of finished gasoline in storage has been attributed to these compounds.¹⁵

Thiophenes are slowly converted by 93 per cent and stronger acid into thiophenesulfonic acids, which are soluble in the acid sludge to about the same extent as the disulfides. They are, however, only slightly affected by 73 per cent acid.²⁵⁷

Pentamethylene sulfide behaves like alkyl sulfides rather than like thiophene.²³

Hydrogen sulfide is oxidized by 93 per cent and stronger acids to elemental sulfur:



Acid of 73 per cent strength has a very slight action. Because of the release of sulfur from hydrogen sulfide, it is desirable to caustic-wash all the distillates which contain hydrogen sulfide before they are treated with acid, as otherwise the oil may become corrosive and require special treatment to remove the elemental sulfur.

Sulfoxides and sulfones are soluble in 93 per cent or stronger acids, and even to some extent in 73 per cent acid.²⁵⁸

Carbon disulfide is not affected by sulfuric acid of any strength: in this respect it is like elemental sulfur.²⁵⁸

Alkyl sulfates, which are formed during acid treatment, are removed in part by fuming and by 93 per cent acid, and to some extent by 73 per cent acid.²⁵⁸ Some of them, however, are retained by the oil. These decompose slowly, even at room temperature, and cause the oils to darken in storage and to separate a small proportion of a brown, viscous, acidic, resinous matter, or gums. On distillation, the alkyl sulfates are decomposed with charring and evolution of sulfur dioxide.³³ This sulfur dioxide is corrosive to the distillation equipment, especially to the condensers where water is present.

Acid esters of sulfuric acid are also formed in treating oils with a relatively large proportion of sulfuric acid (10 to 50 pounds per barrel). They may be retained to some extent in the oil, but as they are removed by the caustic wash, their content in the refined product is negligible.

The amount of the neutral and acid esters can be greatly decreased in treatment by reducing the time of contact between the acid and the

distillate, and by using weaker acid or lower temperatures. Any of these methods lessens the amount of sulfur dioxide formed in the subsequent steam-distillation of cracked distillates and prevents corrosion of the stills and condensers. It is probable that the use of "sludge treatment" or countercurrent treatment, in which the acid sludge comes in contact with fresh oil, is conducive to ester formation in the oil and, therefore, objectionable in this one respect. Nevertheless, the use of the sludge when it is fresh as a substitute for the first fraction of acid in the acid treatment is known to effect a large saving in the amount of acid required. This saving is especially marked in such procedures as the "Stratcold Process."

In contact with sulfuric acid, some of the sulfur compounds in the light oils have a tendency to condense with the unsaturated hydrocarbons and form dye-like compounds. Thiophene and cyclopentadiene may thus form a red dye, and thiophene and cyclohexene a green dye. All these dye-like substances, whatever their color in the free state, form an orange-yellow solution with sulfuric acid.²³¹

Rates of Action of Sulfuric Acid on Various Impurities in Petroleum

Comparatively little work has been done in determining the reaction rates of sulfuric acid on the impurities in oil; but it seems that the acid reacts most rapidly with the amines, amides, and amino acids, then with diminishing activity with the following: asphaltic and similar compounds, olefins, aromatics to form sulfonates, and naphthenic acids.¹⁹⁷ A part of these compounds is always removed during the removal of coloring matter; and new sulfur compounds, such as the alkyl esters, sulfones, etc., may be formed simultaneously.

Classification of Petroleum Products Requiring Sulfuric Acid Treatment

Practically all petroleum products can be refined with sulfuric acid, although the method of treatment and the results obtained are different for the various products. The following types of products are usually given sulfuric acid treatment, though a number of them, such as lubricating oils and kerosene, are now treated more economically with solvents.

(1) Light distillates, such as gasoline and naphtha, obtained directly from the crude oil without recourse to cracking, are usually easy to refine to meet market conditions; the main function of the acid is the improvement of color. Much of the distillates is not acid-treated, but the color and gum content are reduced to an initial low figure by passing the gasoline in the vapor condition through clay (Gray Process) or by other means; then, if necessary, inhibitors are added to prevent color or gum formation.

(2) Distillates cracked at high temperatures are, as a rule, relatively

resistant to chemical treatment and present a special refining problem. This statement does not include distillates produced by cracking oils with aluminum chloride, which is itself not only an efficient catalyst for cracking but also an active refining agent, nor distillates produced by catalytic cracking, such as by the Houdry process, which yields stable products. Sulfuric acid lowers the sulfur content, reduces the gum-forming tendency, and improves the color and the chemical stability of the cracked distillates. The problem of refining cracked distillates is not only different from that of refining uncracked products but is different for products of the various cracking processes. The gasoline from vapor-phase cracking is the most difficult to refine because of its high percentage of chemically reactive constituents.

(3) Kerosene and lamp oils are refined primarily to improve their burning qualities through removal of aromatics and unsaturated hydrocarbons, the degree of refining being measured by the increase in the A.P.I. gravity and by other changes. The elimination of sulfur compounds and improvement in color are often important.²⁵² Kerosene distillates containing large quantities of aromatics are now usually refined more economically by solvent methods.

(4) Lubricating oils can be subdivided into two general groups; distillate stocks and residual stocks. The lubricating oil stocks requiring acid treatment are usually produced from the distillation of asphalt- and mixed-base crude oils. Occasionally the residual oils (cylinder stocks) from the distillation of paraffin-base crude oils require refining with acid. At present the general practice is to refine lubricating oils with solvents,¹²⁶ but the solvent refining is not necessarily the best method for refining all types of oils both in respect to cost and to quality of the products.

The amount of refining required to produce the best lubricating oil varies with the crude oil and with the distillation procedure. As the lubricating properties may be impaired to a certain extent by excessive percentages of acid, it would be preferable to refine these oils to improve their resistance to oxidation and not to refine them to a given color. Individual refineries are obliged to arrive at the optimum proportion of acid by numerous laboratory oxidation tests and particularly by actual engine tests.

(5) Slack wax and crude scale wax are refined in about the same manner as the lubricating oils. Waxes are usually refined for odor and color; a light acid treatment is often sufficient.

(6) Special products, such as cleaners' solvent, solvent naphtha, medicinal oils, "water-soluble" oils, transformer oils, turbine oils, oils to be used in fruit tree sprays, etc., require individual treatment.

The petroleum products, enumerated above, which require acid treatment often demand different refining methods. For this reason, only a general discussion of the various methods is possible. The following rules are, however, fairly definitely established:

(1) Higher-boiling fractions require more severe treatment for a certain degree of refinement than lower-boiling fractions. The proportion of acid needed decreases with the narrowness of the boiling range, and sharply cut fractions are usually considered desirable for decreasing the cost of treating.¹⁶⁸ Entrainment during the distillation process should be avoided.

(2) More viscous oils require more acid than less viscous oils.

(3) Destructive distillation (cracking) produces oils which are more difficult to refine than straight-run products. Cracked oils, even if only slightly cracked during distillation, are much more difficult to refine to good color than those that are not cracked.

(4) The type of crude oil involved and the impurities contained in it determine to a great extent the severity of the chemical treatment; two oils of almost identical physical characteristics may require different treatment.

The efficiency of the acid treatment depends on the concentration of the acid, temperature, time of contact, percentage of acid used, and method of application. These features are discussed in the following pages.

Effect of Impurities or Chemicals in Sulfuric Acid on its Refining Properties

Oxides of nitrogen or nitric acid in the sulfuric acid used in refining have long been known to be detrimental to the color of the finished petroleum product. Nitrous acid is injurious in quantities of 0.02 per cent or higher,⁴⁴ and the maximum permissible concentration for N_2O_5 in the acid is usually 0.05 to 0.07 per cent, a value which is probably a fair estimate, as various investigators agree.¹⁰⁸ In certain rare instances small proportions of nitric acid in sulfuric acid are said to be advantageous. Thus it is claimed that olefins can be effectively removed from light oils which contain aromatics by treatment with sulfuric acid to which one per cent or less of nitric acid is added.²⁰² In this proportion nitric acid will not affect the aromatics. The value of the procedure is not apparent, however.

For certain products in which the final color is not of special importance, greater percentages of nitric acid in the sulfuric acid may be used. Thus, according to one patent, binders or road oils can be manufactured from tars or similar products by heating them to about 375° F. in jacketed containers with 5 to 8 per cent of sulfuric acid and 2 to 3 per cent of nitric acid.²⁴⁵ The use of nitric acid may be economical in treating wax.²⁴⁸

Selenium oxide in the sulfuric acid in quantities greater than 0.05 to 0.07 per cent is injurious to the color of an oil. Moreover, an oil which has become discolored by an acid containing either selenium oxide or nitric acid is then difficult to decolorize by treatment with pure acid. Sulfuric acid containing over 0.005 per cent of selenium oxide turns black when shaken with refined petroleum, and this property can be used as a quick test for selenium oxide in the acid.²⁰⁸

Small quantities of organic matter in the sulfuric acid are permissible. Recovered, or reclaimed, acid, which usually contains considerable quantities of organic substances (1 to 5 per cent carbon content), is used in refining oils without any undesirable effect. In fact, such acids often show a little higher efficiency when used as decolorants for gasoline or kerosene.

The work which has been cited above is based primarily on the results obtained by treating the oil with acid and neutralizing with sodium hydroxide without the use of additional refining agents, such as clay, etc. If such additional treatment is employed, the colored compounds formed in the oils by using acid containing selenium compounds or nitric acid seem to be fairly easily removed, but information is not available to warrant broad generalizations along these lines.

The purity of the acid is seldom a troublesome factor in commercial practice, particularly since by far the greater portion of the acid is now made by the contact process which obviates contamination with the oxides of nitrogen. Other factors in acid refining usually cause considerably more difficulty than the impurities in the acid.

The addition of certain chemicals to sulfuric acid may be beneficial in producing better products. Oils boiled or agitated with dilute sulfuric acid in the presence of an oxidizing agent, such as lead oxide, chromic acid, ferric oxide, or manganese dioxide, are said to be improved in color, but the economy is very doubtful.⁹⁷ Potassium bichromate in the proportion of about 5 per cent by weight of the acid has been patented for the purification of mineral oils of asphaltic origin.¹⁶⁴ A solution of chromic acid in sulfuric acid of 30 to 60 per cent concentration (or a mixture of sulfuric acid and chromium sulfate) has been patented for bleaching montan wax when heated.¹⁹⁶ Chromic acid is said to attack the fluorescent properties of the oil so that complete deblooming is possible.^{4, 247} However, fluorescence is not now considered objectionable except in special oils, such as medicinal and perfumery oils.

A solution of chromic acid in sulfuric acid is said to possess properties similar to those of fuming acid.⁹⁸

It is very doubtful whether manganese dioxide or other manganese compounds as oxidizing agents in acid solution would have any but harm-

ful effects on the color of the oil.¹⁰⁸ Tests made by the writers with such a mixture on cracked gasoline have resulted in very dark products.

Reducing agents may be of some benefit in refining certain petroleum distillates and seem to be of special value in treating cracked distillates for color. Finely divided metallic iron or lead, as well as zinc and similar reducing agents, have been considered valuable when used with the acid for purification purposes.⁴⁸ A patented process specifies that oil, especially kerosene stock, be saturated with sulfur dioxide before it is treated with sulfuric acid,²²³ but no such method has met with any extensive use.

Strong reducing agents cannot be used on distillates which have been "sweetened," *i.e.*, which contain organic disulfides, without turning them sour. The disulfides are reduced to mercaptans.

Phosphorus pentoxide¹²⁹ dissolved in sulfuric acid increases the sulfonation of aromatics, though the quantity needed would doubtless be prohibitive (15 per cent of P_2O_5 by weight of the acid is recommended). Such a reagent, if inexpensive, would be valuable in the treatment of kerosene, especially for the removal of aromatics.

Claims have been made that about 2.75 per cent of boric acid dissolved in sulfuric acid of 93 per cent concentration prevents the sulfonation of aromatics.¹²⁹ Such an inhibitor would be desirable in treating gasolines with acid.

The addition of alkaline and alkaline-earth sulfates to sulfuric acid is claimed in various patents to lessen the energetic action of the acid on the oil, to yield sludge or pitchy residue which can be utilized, and to permit a better recovery of the sludge acid.²¹⁰ For usual commercial practice, about two parts of sodium sulfate to two or three parts of sulfuric acid is recommended.

Treatment of cracked gasoline with sulfuric acid and cupric sulfate has been patented to remove sulfur compounds.⁷³

For sulfur reduction, a reagent formed by the interaction of fuming acid with an excess of benzene or other aromatic hydrocarbons, such as toluene or xylene, has been patented. It is claimed that the removal of sulfur is effected without decreasing the content of aromatic and unsaturated hydrocarbons.¹⁰

In order to accomplish a greater reduction of sulfur in oils, such as those of California, a solution of persulfuric and Caro's acid has been patented.¹¹ The value of these acids in refining gasoline is questionable, however, as the experience of the writers indicates that the results are not better than those obtained with sulfuric acid alone, and the cost is greater.

A mixture of sulfuric acid with olefins, or rather treatment with alkyl

sulfuric acids, is patented for recovering olefins.¹²³ For cylinder stocks, a process recommends treating the stocks with sulfuric acid, then mixing with a lighter petroleum oil and allowing the sludge to settle.¹⁰⁰ Fatty acids may be added to oils in the course of treatment with fuming or concentrated sulfuric acid to purify and deodorize the oils.¹⁸⁹

Treatment with a sulfonated aromatic hydrocarbon at high temperature has been patented.⁹⁴ For refining used lubricating oils, mixtures of acid and oil, which are obtained by mixing sulfuric acid with a fresh oil containing constituents which combine with sulfuric acid (aromatic derivatives, unsaturated fatty oils, and their fatty acids), may be employed.²²⁷

Absorption of ethylene or its homologs by sulfuric acid is facilitated by catalysts, such as silver or silver compounds. Olive oil, castor oil, rape-seed oil, Turkey red oil, chloroform, carbon tetrachloride, Tetralin, carbon bisulfide, and stearic acid have been patented for use in producing emulsions of the gases with sulfuric acid, thus bringing about better contact.⁸⁴

Notwithstanding the large number of substances considered for use with sulfuric acid to increase its efficiency or to make its action milder toward some desirable constituents of the oil, the application of these substances in commercial practice is very limited; doubtless few, if any, are economical. All these methods seem not to have progressed beyond the laboratory stage, and more convincing evidence is required to warrant their use in plant practice, particularly because the action of the acid can be considerably modified by employing less complicated methods, such as changing the concentration, the treating temperature, etc.

Concentration of Sulfuric Acid for Refining

The concentration of sulfuric acid most suitable for treating any individual distillate depends upon the purpose of the refining. In treating light petroleum distillates for color only, often a rather dilute acid is advantageous; but for removing combined sulfur, for improving burning qualities of kerosenes, for removing tar or asphalt from lubricating oils, etc., a strong acid should be used. Inasmuch as concentrated acid con-

Table 9. Loss to Sludge in Treating Crude Lubricating Oil Distillate with Sulfuric Acid of Various Strengths.

Strength of acid (%)	100	97	95	92	87	82	75	71	65
Increase in volume of acid layer (%)	25	23	20	15.5	10	7	5	0	0

verts greater amounts of the oil into sludge than dilute acid, and as the concentrated acid may produce some undesirable changes in the oil, the strength of the acid should not be greater than necessary to give the desired results.

The relative losses of oil to sludge by contacting with acids of different strengths is illustrated in Table 9. This table gives the data obtained in treating a lubricating oil distillate of 0.920 specific gravity (22.3° A.P.I.) which had been diluted with one-half its volume of gasoline. The volume of sulfuric acid was equal to one-half the volume of the heavy oil, and the acid was used in various concentrations.¹⁰⁸

In refining California steam-distilled lubricant stocks to finished automobile oils of average commercial colors without the use of clay, the data of Table 10 are typical.

Table 10. Acid Treatment of California Lubricant Distillates.

	Grade of Oil		
	Light	Medium	Heavy
95% Acid, lb./bbl. (42 gal.)	55	60	60
Saybolt Viscosity at 100° F.	220	350	600
Loss to sludge (%)	25	27	30
Color, A.S.T.M.	3	3	4

When a large amount of steam or a high vacuum is used in the distillation of the stock, less acid is required to yield a given color. The use of decolorizing or adsorbent clays also decreases the amount of acid required. The latter phase is discussed in the chapter on Adsorbents. The use of clay involves extra equipment and loss of oil to the clay.

From Table 9 arises the question of the most economical strength of acid to use, and extensive laboratory experiments are always made by refiners to determine such a factor.

In refining light distillates from asphalt-base crude oils, acid of 85 to 93 per cent concentration is used more generally than acid of any other strength, although 95 per cent acid up to fuming acid is frequently used. Fuming acid is commonly used on kerosene stock containing aromatic constituents and at low temperatures on cracked gasoline to remove combined sulfur. In the extensive application of the cold-treating process, the use of 98 per cent acid is rapidly increasing, and it is preferred to acid of any other concentration. An acid weaker than 85 per cent is seldom used at any temperature although in some instances its use should be encouraged, *e.g.*, in the treatment of a cracked gasoline which contains a high percentage of unsaturated compounds and in which there is but little combined sulfur.

The recent patent of Kendall¹³⁴ uses sulfuric acid of 55-57 per cent concentration to remove the inherent gums without the formation of higher-boiling polymerization products. Such treatment obviates subsequent distillation, but it is not designed to lower the sulfur content appreciably or to render the gasoline colorless.

Brandt and Hougen²⁷ find that cracked gasoline can be refined with

weak sulfuric acid (1 per cent by volume of 25 per cent acid) to yield satisfactory color and color stability without redistillation, provided the gasoline is further extracted with caustic-methanol solution (the solution contains about 13 per cent by weight of caustic soda) with air excluded. If air is present or if aqueous caustic solution is used instead of the methanol-caustic solution, the color of the finished gasoline is much less stable.

The weak acid causes no loss or polymerization of the olefins of the cracked gasoline.

Laboratory experiments and a semi-commercial experiment in a continuous plant have been made.

In practice, at least 90 per cent of the methanol applied to the gasoline separates in the spent reagent and is recoverable by distillation. The remaining 10 per cent of the methanol is substantially completely extracted from the gasoline by the final water wash. The total recovery of the methanol is 99.8 per cent of that used.

The following is a brief outline of general effects of acids of various strengths on different petroleum products.

The percentage and the concentration of acid used in treating distillates from paraffin-base oils are entirely different from those used in treating the distillates from asphalt-base oils, especially cracked gasoline and all the straight-run products above the gasoline fractions. The kerosene stock from asphaltic crude oils is rich in aromatic compounds and compounds with a comparatively high ratio of carbon to hydrogen, all of which burn in a lamp with a smoky flame and which are most economically removed by fuming acid or by extraction with liquid sulfur dioxide. The kerosene from paraffin-base oils contains no such compounds.

The lubricant stocks from asphaltic crude oils contain chemically unstable and potential asphaltic materials, which must be removed; and until the recent advent of certain types of solvents, strong or fuming sulfuric acid has been much the most economical reagent for this purpose, clay or adsorbent alone being entirely unsuitable. No such impurities exist in paraffin-base lubricant stocks, and a small proportion of sulfuric acid of 93 per cent concentration, or even weaker, or adsorbent material is sufficient to fit them for service.

Almost all cracked gasoline from asphaltic stock is rich in sulfur compounds, and as yet the only practical method known for their removal is the use of strong acid, preferably at low temperatures. For the removal of combined sulfur from petroleum products, it is found that 93 per cent acid (66 Bé.) is very roughly about 60 per cent as efficient as fuming acid (103 per cent acid); and for improving the burning quality of kerosene stock from asphaltic crude oils, about the same relationship holds,

although different stocks may show large variations from this factor. The foregoing comparisons do not imply, however, that the overall refining action obtained by the use of acid of a certain strength can be exactly reproduced by employing smaller or larger quantities of stronger or weaker acids. For instance, in treating for color the optimum concentration of the acid is different from the concentration necessary to obtain a certain sulfur content, and, therefore, comparisons are possible only on the basis of a given property of the refined product and not on the basis of its overall quality.

An acid of 40 per cent concentration has a slight polymerizing and slight dissolving action on oils, especially on cracked distillates.⁸¹ For some special purposes, such as the removal of nitrogen bases or for flocculating the asphalt in the crude oil,⁶⁴ even a considerably greater dilution can be used. Acid below 78 per cent strength, preferably about 60 per cent, is recommended as a polymerizing agent for the reactive compounds in certain oils;⁶⁰ the polymers, being insoluble in the sludge produced, remain in the oil. After treatment with an acid of this concentration, the oil is distilled, and the polymerized products, recovered as still bottoms, are considered suitable for use in varnishes, etc. In using dilute acid, especially at high temperatures, there is danger of leaving sulfonated products in the oil, as they are not dissolved by the weak acid. A weak acid (60 per cent or less) has practically no desulfurizing action on oils. In refining hydrocarbon oils of origin other than petroleum, a dilute acid is almost always preferable to a strong acid.

A process for treating vapor-phase gasoline has been developed by the Laboratory of the Royal Shell Group.¹⁴⁰ It consists in treating the gasoline successively with sulfuric acid of 30 per cent strength at normal temperature, then with 70 to 80 per cent acid at 122° to 302° F., and finally with 40° Bé sodium hydroxide solution.

Some of the unsaturated compounds can be removed from tar distillates, containing chiefly benzene, toluene, and solvent naphtha, by treatment with 70 to 75 per cent acid.¹⁸

Beard¹⁴ has summarized the action of sulfuric acid on various gasoline constituents.

Although acid of less than 60 to 70 per cent concentration has very little effect on oil, acid of 70 to 83 per cent strength can be used in the refining of many light petroleum distillates, especially for decolorization purposes. An 80 to 85 per cent acid can be used in decolorizing cracked or straight-run petroleum distillates. The color of the products refined with an extremely weak acid is often less stable than that obtained with a stronger acid, such as 83 to 93 per cent; but this difference is not always true, and at times a moderately weak acid may be found to be efficient for treating oils to good and stable color, whereas a more concentrated acid is more efficient if only an intermediate color is desired. The appli-

cation of acid in a countercurrent treating system for decolorization purposes is economical; but the used acid, or acid sludge, must be re-used while it is fresh, preferably within an hour or two. Treatment for color in gasoline is of little importance now, especially if the gasoline is to be dyed to some desired color.

With a certain cracked distillate, acid of 10 to 30 per cent concentration had scarcely any effect at all. Above 40 per cent concentration, the temporary darkening of the distillate from the acid sludge formed within the oil was in proportion to the concentration of the acid. Between 50 and 60 per cent, a diminution in the volume of the oil began to be measurable. Acid of 70 per cent strength dissolved half as much as 85 per cent acid. The maximum absorption of the oil by 85 per cent acid required $1\frac{1}{2}$ to 2 volumes of the acid to one of oil.⁸¹ The acid of this high dilution is economical when repeatedly used. However, refining cracked distillates with weak acid is often desirable.³⁰

An acid of 65 to 93 per cent concentration is used in preparing alcohols from cracked vapors,¹⁵⁶ though a more concentrated acid can often be used for this purpose.²⁰¹ An acid of 90 to 100 per cent strength usually has a very different effect on an oil from that of 70 to 80 per cent acid.¹⁷

For certain special purposes, such as producing alcohols, the oil can first be agitated or emulsified with water and then the acid gradually added at a temperature of 60 to 70° F. until the desired maximum concentration of the acid is reached.¹⁵³

Acid of 98 per cent concentration is used extensively in refining lubricating oils.²⁰⁰ In most instances these oils are treated more effectively with this strength of acid than with weaker acid. The use of fuming acid on such oils may not be desirable because of its oxidizing tendencies.

Fuming acid is more economical for refining many petroleum products than weaker acids. It generally is used with a content of about 15 to 20 per cent of sulfur trioxide. High-grade kerosenes from asphaltic crude oil are refined with fuming acid unless the liquid sulfur dioxide method of Edeleanu is used. Certain types of transformer oils, as well as many heavier petroleum distillates, which require drastic refining, are treated with fuming acid.⁵⁰ Complete deblooming of oils has been possible only by treatment with fuming acid. The use of the fuming acid is therefore necessary in the production of medicinal oils. Spray oils, or miscible oils used as insecticides on foliage, are refined with fuming acid or with fuming acid and liquid sulfur dioxide.

Fuming acid does not, as a rule, give the best color to any of the commercial oils, since it oxidizes the less stable hydrocarbons more extensively than 98 per cent acid or still weaker acid. A considerable quantity of sulfur dioxide is always evolved when fuming acid is used at normal temperatures. Many of the oxidation, and perhaps sulfonation, products

resulting from the fuming acid treatment are soluble in the oil and are responsible for the poorer color of the finished product. As some of these colored substances seem to be more soluble in 93 per cent than in fuming acid, it is sometimes advantageous to agitate the oil with small amounts of 93 per cent acid after it has been treated with fuming acid, in order to produce better color. It is also not uncommon, when several applications of acid are to be made, to use acid of different concentrations in the successive applications. Weak acid may follow application of strong acid for the reasons mentioned above, or the weak acid may precede strong acid in order to remove some of the undesirable constituents without excessive sulfonation. In the treatment of lubricating oil distillates, it is the usual practice to use 98 per cent acid first and then fuming acid. The use of 98 per cent acid in quantities above a certain amount is not so economical as fuming acid because of the tremendous quantities of the former that are required. Fuming acid is employed if the quantity of 98 per cent acid needed would be excessive, such as 50 or more pounds per barrel.

Cracked distillates may be treated first at ordinary temperatures with dilute sulfuric acid (*e.g.*, 30 per cent strength) and then at 15-25° F. with a strong acid (*e.g.*, 98 per cent strength). Lewis¹⁴⁶ follows the treatment at the low temperature by treatment with strong acid at normal temperature and then steam distills.

The direct use of sulfur trioxide has been considered for many years; but it is seldom, if ever, used on a commercial scale. Sulfur-containing and smoke-producing substances in lamp oils can be removed by treating them, especially those from asphalt-base crude oil, with sulfur trioxide or with sulfur trioxide diluted with an inert gas.²² The process has been patented for desulfurization and purification of cracked gasoline,⁹³ but apparently it has not been used. Distillation of the oil in contact with sulfur trioxide has been patented for the removal of sulfur compounds, particularly from kerosene.²²² The bleaching and decolorizing action of sulfur trioxide on petroleum oils is the subject of a very old patent.¹⁰³

The strong oxidizing properties of sulfur trioxide prevent its general use except at low temperatures and in very special products, and then only on oils that are quite stable chemically. It is too severe in action on cracked products.

The quantities of sulfur trioxide required for the separation of resinous substances from a certain crude petroleum, kerosene distillate, and middle oil distillate, were 2.2, 0.2, and 6.2 per cent, respectively; whereas the quantities of sulfur trioxide required for the production of saturated compounds were 45 per cent in the crude petroleum, 3 per cent in the kerosene, and 24 to 25 per cent in vaseline, transformer oil, and machine oil distillate.¹⁰⁰ As the losses in treating oils with sulfur trioxide are greater than with sulfuric acid, the use of sulfur trioxide is certain to be limited exclusively to oils which do not contain appreciable quantities of "unsaturated" compounds.²⁴³

Experience shows that the choice of the concentration of the acid is determined by its selective action on the specific constituents of the oil which are to be removed. Some of the constituents are entirely unaffected by acids of relatively low strength. In other cases, very large quantities of a weak acid would be required. It is stated, for instance, that 6 per cent of 92.3 per cent acid diminished the unsaturated content in a Baku distillate to the same extent as 10 per cent of 90.2 per cent acid.¹⁰⁵ However, the refiner must usually be content to choose the concentration of the acid which will leave the valuable constituents unaffected and partly remove the objectionable ones.

Quantity of Acid Required

The maximum proportion of sulfuric acid used in practice is limited by the following considerations:^{4, 247}

(1) The degree of refining as indicated by the normal means of measuring the effects produced is not proportional to the amount of acid used. This is shown by the "true" color data of Table 11 and the sulfur data of Table 12, as well as by other changes.

Table 11. Treatment for Color.

Quantity of 93% Acid (Per Cent by Weight of the Lubricating Oil)	Color of the Refined Oil	
	A.S.T.M. Scale	True Color Scale
5	5	73
10	3	12
15	2	4.8
20	1½	1.2
50 (including 30% of fuming acid)	1	0.44

In Table 12 the loss of oil to sludge is by no means proportional to the removal of the sulfur but is somewhat proportional to the amount of acid used. This ratio of loss of oil to sludge does not exist in still heavier treatment but becomes less and less with larger amounts of acid and with

Table 12. Treatment at Normal Temperatures for Sulfur Reduction in Cracked Gasoline from California Heavy Gas Oil Followed by Steam Distillation.¹⁶⁷

93% Acid (Lbs. per Barrel)	% Sulfur in Refined Product	% Loss of Stock Based on Gasoline Treated
0	0.88	0.0
8	0.61	2.9
20	0.32	7.9
30	0.24	14.4
40	0.19	19.1

the elimination of the chemically reactive compounds. A different oil would show a different behavior for both sludge loss and percentage reduction in sulfur. See later tables in this chapter.

(2) Too much acid applied in one charge to lubricant stock may, if heating is not prevented, "burn" the oil, or give it a permanently dark color. This condition is doubtless due to oxidation of the oil by the acid and is accompanied by the evolution of an excessive amount of sulfur dioxide. The remedy is to cool the oil or to add the acid in small charges, preferably in the form of a spray. This problem will be discussed in more detail in connection with the temperature of treatment. If the oils become "burnt," they appear brownish or bluish in color. The pleasant "outer tone" is destroyed. The range for the quantity of acid which can be used without injury to the oil is rather wide. Proper temperature control permits the safe use of very large quantities of acid.

(3) The more viscous the oil, the more readily it emulsifies, and the greater the danger of forming a stable emulsion with the acid. An emulsion is always a serious problem, and when broken it almost always yields a darkened oil because of the long time of contact between the oil and acid sludge.

If insufficient acid is used on a lubricating stock, not all the undesirable substances are removed from the oil. Moreover, the oil will retain its raw or crude oil odor, and it will darken on standing. If very little acid is used on any oil, a substantial increase in the sulfur content will occur through formation of dialkyl esters which remain dissolved in the oil.⁶⁶ A larger percentage of acid removes these substances.

The resistance of a given distillate to chemical treatment for color is not constant but varies with its age (or the time it has been in storage). An aged oil may become either more easy or more difficult to treat, and this factor of change is frequently utilized with economy in a refinery. Some plants prefer to treat gasolines immediately after they are produced, even if they are to be placed in storage. The initial color of this gasoline may be considerably above specifications in order to allow for reversion of color on standing. However, the quantity of acid used is often less than that required for treating aged distillates to specification color at the time when the gasoline is sold. This condition applies especially to cracked and to straight-run gasolines, but similar observations have also been made on some lubricating oil distillates.¹²⁸

In general the amount of acid required depends both on the character of the oil and the degree of refinement desired; it is impossible to predict the amount of acid needed without making preliminary tests; and as the character of the distillate produced at the same refinery is not uniform, it is seldom possible to construct a table or a chart accurately anticipating the effect of various quantities of acid. The following data give, therefore, only a rough approximation of the quantities of acid which are used in refining. It should be noted, however, that if heavy treatment

is required for a given effect, it is now more economical to substitute solvent refining for at least part of the acid.

Natural gasoline (casinghead) usually requires no acid but sometimes as much as 2 to 5 pounds per barrel.

Straight-run gasoline requires 0 to 3 pounds per barrel.

Cracked gasoline requires 2 to 6 pounds per barrel for color and gums. Cracked gasolines from California and Mexican crude oils require more acid than those from Mid-Continent and especially those from Eastern crude oils. The figures which are given do not take into consideration the extensive removal of sulfur, as the desulfurization of certain cracked gasolines requires almost prohibitive quantities of acid. If the cracked gasoline is to be treated for color and gum only, decolorizing clays alone are now often used, and then the gasoline is made more stable chemically by the addition of small amounts of inhibitors.

Various solvents may require up to 5 pounds per barrel, but usually none.

Kerosene requires 1 to 75 pounds per barrel, depending on the degree of refining desired. Kerosene from asphalt-base crude oils usually requires more severe treatment than that from other crude oils. Treatment with as high as 75 pounds or more of acid per barrel is, therefore, not uncommon at certain refineries, although kerosene stock of this type is now usually refined with liquid sulfur dioxide, as described in the chapter on Solvent Refining.

Lubricating oils require 0 to 60 pounds per barrel. Oils intended for very severe conditions may require much larger amounts. Oils from asphalt-base crude stock require much more acid than Mid-Continent and especially Pennsylvania oils. The latter are often not treated with acid at all. Residual oils require, as a rule, larger quantities of acid than distilled oils. Most of the lubricating oils of recognized brands are now prepared by solvent refining and with little or no sulfuric acid. The products are superior to those obtained by the straight sulfuric acid refining, and the cost is lower.

Transformer oils require 0 to 100 pounds or more of fuming acid per barrel, depending on specifications. In treating for a low German Tar Number, only a little acid is used because larger quantities impair the oxidation stability as measured by this test. In treating for a low Michie oxidation test, large quantities of acid should be used.

Wax usually requires from 0 to 30 pounds of acid per barrel. However, quantities as high as 300 pounds per barrel are specified in some patents.²⁴⁹

"Water-soluble" and spray oils for citrus trees require at least 200 pounds of fuming acid per barrel to give low "unsaturation."

The insecticidal properties of untreated petroleum products are much higher than those of the refined products, but such raw products are too toxic to foliage for practical use. When petroleum spray oils came into prominence a few years ago, it was shown by Gray and De Ong¹⁰⁰ that the relative toxicity of the various oils to foliage was roughly proportional to the amount of "unsaturates" in the oils, the "unsaturates" as used here meaning any of the chemically active constituents of the petroleum that can be extracted or removed from one volume of the oil by four volumes of 98.6 per cent sulfuric acid at 203-212° F. in one hour. (Method of the California State Department of Agriculture.)

Tucker,²³⁸ chemist of the California State Department of Agriculture, finds that these chemically active constituents of the petroleum are not in themselves toxic to the foliage but become so through their oxidation, catalyzed by sunlight; that is, if the film of untreated oil on the foliage is completely shaded from light, it is not toxic to the foliage. Tucker's data show that some of these reactive constituents in the untreated petroleum oils are first oxidized into complex carboxylic acids (asphaltogenic acids) and then apparently into colloidal asphaltic compounds. The oil becomes toxic to the foliage when about 0.5 per cent of the asphaltogenic acids is formed.

Because of the potential injury to foliage, these spray oils are manufactured with the greatest of care; and in the severe test with hot sulfuric acid noted above, no over 5 to 15 per cent of the oil is soluble in the acid, or, expressed differently, the unsulfonated residue from the test is from 85 to 95 per cent.

Experience with these spray oils shows in an empirical way that the constituents which can be dissolved by the concentrated sulfuric acid, or first oxidized by the acid and then dissolved by it, are those that become oxidized under the catalyzing influence of sunshine and become toxic to the foliage. Weather conditions—temperature, brightness of the sunshine—obviously greatly influence the behavior of these sprays on the foliage.

The highly refined oils, though not so toxic to the insect pests as the unrefined oils, are still amply effective.

Medicinal oils require 200 pounds or more of fuming acid per barrel. They are now prepared at some refineries with the aid of solvents.

Methods of preparing medicinal and white oils have been published. Kauffman¹³¹ gives a good description of refining medicinal oils with acid. About 130 pounds of acid per barrel of oil is applied in five fractions.

In Germany the Baku distillates are employed for manufacturing white oils.¹³⁰ From 45 to 50 per cent of fuming acid by weight of oil is used. The acid is applied in about five per cent portions and with air agitation. The oil is then neutralized with 25° Bé sodium hydroxide solution, washed three to five times with water until neutral, dried with air, mixed with 1.5 to 3 per cent floridin clay, and filtered.

The Standard Oil Company of New Jersey treats medicinal and similar oils in a continuous system by applying the acid countercurrently. Solvent refining is now displacing the use of a large portion of the acid.

According to one American patent,²²⁴ medicinal oils are successively treated with fuming acid, with 88-90 per cent acid at about 170° F., and finally with adsorbents. In another process,¹⁷⁵ 25 to 35 per cent of fuming acid by weight of oil is used at 120-140° F., special emphasis being laid on securing the maximum quantity of sulfonates from the refinery operation.

Nugey¹⁷⁰ reports on the methods and costs of manufacturing the white oils.

The technical grades of white oils differ from the medicinal grades only in that the removal of the sulfonatable portion of the oil is not quite so complete, and the viscosities are usually below 200 seconds Saybolt at 100° F.

In determining the economical quantity of acid required for treating an oil, it must be remembered that over-refining of the oil may remove

or destroy some of its best properties. Thus in refining gasolines, as mentioned before, valuable aromatic and unsaturated hydrocarbons are removed. Similarly the properties of lubricating oils are somewhat injured by a large quantity of acid. The characteristics of the finished product, as usually demanded, such as color, odor, etc., have no practical value and may not give any indication of the actual lubricant qualities of the finished oils. Application of excessive quantities of acid in refining turbine and transformer oils yields products which may develop high acidity in use.

Temperature of Treatment

The temperature is exceedingly important in refining with acid. The proper temperature depends on the specific purpose of the refining. A general discussion of the effects of temperature on the acid treatment of oil follows.

High temperatures favor removal of aromatic and unsaturated hydrocarbons and the bituminous and asphaltic substances.

The amount of oil per pound of acid lost as acid sludge is not greatly different for normal temperature and low temperature treatment. The kind of oil and its viscosity, as well as the methods of settling or isolating the sludge, make some differences in the losses reported by various experimenters. Morrell and Egloff¹⁷¹ measured the relative amounts of the acid sludge produced in treating cracked gasolines at normal and at low temperatures with varying quantities and concentrations of sulfuric acid. They find that the loss per pound of acid used is a little greater at normal or higher temperatures than at low temperatures.

In a different set of experiments on cracked gasoline, shown later in Table 16, the loss of oil per pound of acid is about the same for normal temperature and low temperature treatment.

However, in the cold treatment of cracked gasolines, less acid is commonly required for desulfurization than in normal temperature treatment, and consequently there is considerably less loss of oil to acid sludge in the cold treatment.

The settling rate of sludge is generally greater at higher temperatures because of the decrease in viscosity of the oil, but in treating some of the non-viscous distillates, the opposite effect may be true. For instance the acid sludge from some California kerosenes settles rapidly and completely at temperatures below 100° F., whereas at 120° F. its separation from the oil presents considerable difficulty. Similar observations have been recorded in treating Galician uncracked kerosenes.¹⁰⁸ Table 13 shows the general influence of temperature in refining this kerosene with sulfuric acid.²⁶⁴

Table 13. Treatment of 1 Liter of Kerosene Stock with 50 Grams of 93% H_2SO_4 (17.5 Lb. per Barrel).

Temp. °F.	Acid Sludge (Grams)	Unused Acid (Grams)	Sulfonic Acids Calculated as H_2SO_4 (Grams)	Polymeri- zation Products (Grams)	Acidity of Kerosene as H_2SO_4 (Grams)	Color (mm.)
32	61.6	47.91	1.45	5.25	0.86	193
41	62.0	46.82	1.55	5.02	1.42	166.5
50	62.5	46.53	1.65	5.13	1.56	143.0
59	63.5	45.72	1.93	5.40	1.76	112.5
68	64.3	44.37	2.22	4.93	2.45	89.5
77	64.8	43.52	2.68	5.62	2.63	80.5
86	65.2	41.87	3.72	5.43	3.65	52.0
95	65.8	40.42	4.90	6.18	4.15	yellow
104	66.0	39.03	5.62	5.78	4.83	yellow
113	66.4	38.62	5.76	5.21	5.62	yellow
122	67.0	37.26	4.81	4.81	5.91	yellow

This table shows that at high temperatures sulfuric acid is more completely consumed and that the process of sulfonation becomes particularly rapid.¹¹⁶ The formation of "polymerization" products in this oil is, on the contrary, almost independent of the temperature. However, it is to be observed that the term "polymerization" is often loosely applied in the petroleum industry, frequently being used to include the sulfonation products, the alkyl sulfates, and all other reaction products which have a higher boiling point than the final boiling point of the distillate before it is contacted with the acid. Zaloziecki²⁶⁴ defines the polymerization products of Table 13 as the "tar" in the acid sludge which can be released from the sludge when the latter is diluted with water, the tar being formed by the action of the acid on the unsaturated compounds of the kerosene distillate. Brooks and Humphrey³³ point out that the early petroleum industry practically universally accepted the theory that olefins in distillates were polymerized by the acid to tars and completely removed from the oil by the acid. The kerosene under discussion here was uncracked and could not form an appreciable amount of true polymers characteristic of the unsaturates (olefins) when contacted with acid.

The color of the oil is considerably better when the oil is treated at the lower temperatures. The data of this table are of general information, although a different stock would certainly give different results. Unfortunately the data do not show the amount of the acid that was reduced to sulfur dioxide, especially at the higher temperatures.

When gasolines and kerosenes are treated in the average refinery at normal or low temperatures with sulfuric acid, the sludge immediately isolated, and the acid content determined by alkali titration with phenolphthalein as indicator, the results show a very high percentage (usually 90-93 per cent) of the original acid present as titratable acid. Such an analysis can be used in continuous operations as a fairly close routine control of the amount of acid being supplied to the oil. A convenient method is to collect a 100-cc. sample of the mixed acid and oil a little distance beyond

the mixing device, agitate it with 25-50 cc. of water, add phenolphthalein indicator, and titrate the whole to a definite pink endpoint. If the strength of the alkali solution is 5.5 normal, each cc. of the solution required represents approximately one pound of acid per barrel.

The rates at which the acid in the acid sludge is reduced to sulfur dioxide and the total amount of sulfur dioxide evolved from the acid sludge on heating have been determined in certain sludges. Stagner²²⁰ has reported the rates of sulfur dioxide formation in samples of cracked gasoline treated at normal temperatures with 93 per cent sulfuric acid. The laboratory sample was treated by the batch method with the acid in one addition. The refinery sludge was a product of a two-stage counter-current treatment of the cracked gasoline with approximately 14 pounds of 93 per cent acid per barrel of the gasoline. In this two-stage method fresh acid was applied to stock already treated with once-used acid, and the sludge resulting from this fresh acid treatment was then used in making the first-stage treatment on new stock.

It is possible that the formation of the high percentage of sulfur dioxide during the first 24 hours in the refinery acid sludge is a function of the countercurrent treatment, but this assumption was not definitely established.

These data are illustrative only of the instability of acid sludge from 93 per cent acid and typical cracked gasolines. The rate of formation of the sulfur dioxide would be lower with a weaker acid and higher with a stronger acid. The effect of the stronger acid would be evident even if the acid was used at lower temperatures and the resulting sludge brought up to normal temperature and permitted to stand.

Portions of each sludge were diluted with about ten volumes of water after they had stood for the respective periods of time indicated in Table 14. The sulfur dioxide was then expelled by boiling, and its quantity determined.

Table 14. Spontaneous Reduction of Acid in Cracked Gasoline Sludges to Sulfur Dioxide.

Age of Sludge ^a	Laboratory Sludge, SO ₂ Based on Fresh Acid (%)	Refinery Sludge SO ₂ Based on Acid Titrated in Sludge (%)
1 hour	1.01	...
4 hours	2.77	...
5 hours (approx.)	...	10.39
8 hours	3.91	...
1 day	7.13	12.26
2 days	8.41	12.49
3 days	9.64	...
6 days	12.09	...
8 days	...	12.86
12 days	13.68	...
21 days	15.79	14.58

^a Sludges were from 66° Bé. acid (approximately 93%) and at normal temperature treatment.

Since the color and the sulfur content are usually of primary importance, petroleum distillates, with the exception of kerosenes and some other products, are generally treated at as low a temperature as possible; but when the color or the sulfur content is of secondary importance to the removal of asphaltic and bituminous substances or aromatic and unsaturated constituents, the distillates are preferably treated at normal or higher temperatures. Moreover, if the distillate, whether straight-run or cracked, is redistilled subsequent to the acid treatment, the final color is not improved by treating below 60 to 70° F. with the acid.

Some patents refer to desulfurization of oils with acid at 110° F.¹⁰ or higher. Pierce¹⁰¹ reports that in treating cracked gasoline at the Louisiana Refining Corporation, the reduction in the sulfur content is slightly greater at higher temperatures, but the color is decidedly poorer. Such data for sulfur reduction at higher temperatures are true only for relatively light acid treatments.

In treating lamp oils, preheating of the oil and of the acid before treatment has been recommended so as to apply the acid to the oil at temperatures above 212° F.¹⁰⁴ Processes have also been proposed for converting tar into pitch by distilling the tar with a limited amount of sulfuric acid.¹⁰⁴ High-temperature treatment, followed by extraction of the oil from the acid residue with benzene or naphtha, is specified, and other similar procedures have been patented.¹¹¹

Refining of oil vapors with sulfuric acid, sulfur dioxide, or chlorine was recommended long ago.⁸⁵ Other processes refer to the use of sulfuric or hypochlorous acid or similar reagents for oxidizing unsaturated hydrocarbons in cracked oil in the vapor phase.¹⁰⁴ Such a method has been patented for refining benzene.²¹⁷ A number of processes was likewise early proposed for desulfurizing oils by distilling them with sulfuric acid.¹⁰⁵ Distillation with sulfuric acid, alkalis, or phosphoric acid is a subject of other patents.¹²⁰ Distillation of crude oil with a mixture of sulfuric acid and an absorbent ("Filtrol") in successive stages and at increasing temperatures up to coking temperature has been specified.¹²⁵

The approximate temperatures maintained in treating the various petroleum products are given below. They are not in any sense strictly followed, and the different refineries usually determine the temperatures that give the best utilization of the acid and best effect on the oil.

In the mild refining of straight-run gasolines, the normal temperature of 70 to 90° F. is most practical. It is not economical to cool the oil below this temperature, and at higher temperatures the oils may become discolored.¹⁹ A range of from 50 to 70° F. gives better colors than from 70 to 90° F.²⁴⁰; but if much acid is used, even 32° F. may be economical.²¹² Water-cooled jacketed tubes can be used to control the temperature in treating,¹¹² as considerable heat is generated during the mixing if a large amount of acid is used.

As mentioned above, sulfonation of aromatics and esterification of unsaturated compounds proceed more readily and with greater economy of acid when stronger acids and higher temperatures are used. Therefore, if high-grade kerosenes are to be made from stocks rich in such

compounds, the stocks are refined with fuming acid and, if possible, at warm temperatures. The temperature should not be excessive, as otherwise the color will be injured. In actual practice the temperature is seldom permitted to go above 130° F. unless the oil is to be redistilled. Preliminary heating of the oil to about 200° F. is specified in one patent on the refining of California kerosene,¹¹³ but the heat generated by the reaction between the oil and acid is absorbed by a cooling medium so as to prevent the temperature from rising substantially above 210° F. In such high-temperature treatment, subsequent distillation is necessary for good color. It was found that in treating a certain kerosene at 95° F. without subsequent distillation, the amount of acid needed for a given color was twice as much as in treating at 70° F. On the other hand, there is often nothing gained in color by treating below 60° F.¹³⁷

To make California and Texas kerosenes burn without clouding the chimney or smoking, it has already been noted that the oil must be treated to eliminate the compounds bearing a high ratio of carbon to hydrogen, such as the aromatics or unsaturated compounds if any are present. Any catalyst which would increase the efficiency of acid in sulfonating these compounds, and thus removing them, would doubtless have economic value. The efficiency of acid in the refining of any given kerosene stock for the improvement of burning qualities can be measured by the change in gravity of the oil or by the change in the boiling point curve when plotted against the gravity, or by the so-called "ring number" of the kerosene, since the boiling points are correspondingly low when aromatics are present and rise when the aromatics are removed.

Some special oils, such as "water-soluble" (miscible) oils, are also preferably treated hot. Here again the compounds having a high ratio of carbon to hydrogen are to be eliminated.

Treating temperatures above 212° F. are sometimes specified.²⁴ Heating crude oils with aqueous acid or sulfonated aromatic hydrocarbons has been patented for purification purposes.⁹¹ Petroleum jelly may be prepared by treating petroleum residues, etc., with sulfuric acid at high temperature; for example, the crude oil is said to be treated with fuming acid for 24 hours at 158° F. and then for 48 hours at 320 to 338° F.¹⁴² It might be added here, however, that fuming, or even concentrated, sulfuric acid would be reduced quantitatively to sulfur dioxide at such a temperature.

In refining lubricating oils for color, the temperature is to a great extent kept as low as the settling rate of the sludge will permit, especially with oils of high viscosity. If the oil is refined to give resistance to oxidation only and not primarily for color, somewhat higher temperatures are economical,²⁴⁰ but even here the refining for resistance to oxidation can be carried out with more accuracy and certainty at lower temperatures. Thus in order to obtain the desired results with an American spindle oil,

the quantity of acid at 65 to 75° F. can be varied within considerably wider limits than at 120 to 140° F.

The usual temperatures for treating the various lubricating oils are controlled mainly by the viscosity considerations; they are shown in Table 15.¹⁸⁰

Table 15. Treating Temperatures of Lubricating Oils.

Viscosity of Oil at 100° F. (Seconds Saybolt)	Temperature of Oil when Acid is Added (° F.)	Temperature of Oil and Wash Water During Washing and Settling Period (° F.)
50	70- 80	110-120
75	80- 90	120-130
100	85- 95	130-140
150	90-100	140-150
200	95-105	150-160
300	100-110	155-165
500	105-115	160-170
1000	110-120	165-175
1500	110-120	165-175
2000	115-125	170-180

Cylinder stocks and long residuum require higher treating temperatures than distillates because of their higher viscosity. They are usually treated at 130 to 170° F., or even at 180° F. If distillates containing wax are treated before the wax is removed by chilling and pressing, the temperature is also preferably kept at a higher level, as wax tends to form emulsions at low treating temperatures.

Temperatures of about 180° F. may not be excessive in certain instances.

As a modification of the treating procedure, the oil may be mixed cold with concentrated acid and then gradually warmed for several hours to obtain a temperature of 122 to 140° F.²⁵⁰

If the temperature is too high, the oil is discolored and the color cannot in general be improved by further warm acid treatment.¹⁹ In some cases, a further cold acid treatment or other treatment, as with clay, may restore the color.^{33, 247} Too low a temperature in the acid treatment of lubricating stocks may give dark color, probably because the high viscosity of the oil prevents proper contact as well as proper separation of the acid sludge and tar.²⁰⁶ These data show that there is a certain optimum range for each lubricating oil stock which should be used. The susceptibility of the stocks to the influence of temperatures of treatment varies. For instance, a Mid-Continent residual stock of about 150 Saybolt Universal Seconds at 210° F. can be treated satisfactorily with acid within a temperature range of roughly 110 to 200° F. However, with Pennsylvania stocks of the same viscosity the temperature range is shortened to about 140-160° F., and in addition a number of other pre-

cautions should be taken during treatment to insure a satisfactory product. Because of these complications some refiners incorrectly believe that Pennsylvania residual stocks cannot be treated with sulfuric acid.

The foregoing discussion of the treating temperatures refers only to temperatures at which the oil is contacted with the main portion of the acid. After most of the sludge is removed from the oil, the handling of the stock is considerably less influenced by the temperature changes; warming to relatively high temperatures during the settling of the last traces of sludge may be beneficial, and is often done. Such procedures frequently lead to a better color of the oil. In certain refineries the oil, such as Mid-Continent, is even distilled in the sour state subsequent to the acid treatment without being neutralized with caustic and shows no harmful effects. The resulting residual oil, although dark in color, apparently requires no more clay for color than if the stock had been neutralized before it was distilled. It may be noted that the oil at the temperature of distilling would reduce the sulfuric acid to sulfur dioxide and thus actually destroy the sulfuric acid. The oil oxidized or charred by the acid would be left behind in the still or would be adsorbed in the subsequent treatment with clay.

It should be remembered that petroleum products in contact with sulfuric acid at a relatively high temperature readily reduce the acid to sulfur dioxide. It is on this principle that the Chemical Construction Corporation regenerates the sulfuric acid used in refining oil. When the acid sludge is heated to about 400° F., the hydrocarbon material in the sludge reduces the acid to sulfur dioxide almost quantitatively. The sulfur dioxide is then catalytically converted into fresh concentrated sulfuric acid, as described in the next chapter.

Processes have been recommended for decomposing the emulsion-inducing compounds in lubricating oils by heating the acid-treated oils to temperatures as high as 650-900° F., which treatment may be followed by washing with dilute acid.¹⁰

In order to treat viscous oils, such as steam cylinder oils, at lower temperatures, the oils may be diluted with naphtha to lower the viscosity.¹⁶² Some refineries handle viscous residual stocks in solution in naphtha throughout the whole chemical refining cycle and then distill the naphtha from the refined oil. This procedure is not generally recommended unless preliminary experiments show that real benefits are to be gained because the high temperature necessary to expel the naphtha may injure the color of some steam cylinder oils, particularly those of Pennsylvania type. Theoretically, dilution is also undesirable, as more acid is required to treat a diluted than a non-diluted stock because of lower concentration of impurities in the diluted stock. The procedure is also expensive because it involves additional distillation and losses of naphtha.

If the dilution is resorted to, it is often preferable to treat the stock first without dilution and then, after separating most of the sludge, to dilute it with naphtha and settle the rest of the sludge. The naphtha should then be distilled at as low a temperature as possible and with the aid of a large quantity of steam or a vacuum to prevent discoloration of the oil.

In preparing lubricating oils procedures contrary to those of dilution are frequently employed. The residuum is first distilled, and then the distillate and the resulting residuum are treated separately with acid. The products are then blended to viscosity specifications.¹³⁸ This method permits the more advantageous use of the different quantities of acid necessary for refining the distillate and the residual fractions than is possible in treating them together. The treating losses and the acid consumption are usually reduced, but the procedure should be properly evaluated before it is adopted.

The use of propane under pressure instead of naphtha for diluting the heavy oils for treatment has been developed. Although the pressure equipment makes the process expensive, its installation may be justified because of a reduction in the quantity of acid required and because of the improved quality of the oil. Treatment in propane solution is described in the literature¹³⁷ and will not be repeated here.

Lubricating oils may be treated first with acid at a relatively high temperature and then at a lower temperature with additional quantities of acid.⁷⁴

Suggestions have been made that the crude oils be refined with acid instead of the residual lubricating oils, as is the customary practice.²⁵⁹ Although in isolated instances the process may be found economical, it appears doubtful whether it will find wide application because of the necessity of giving a uniform treatment to all the fractions and the possibility of damaging the oil during subsequent distillation.

Transformer oils are best refined at 60 to 65° F., but a temperature of 85 to 90° F. may not be prohibitive.⁵³ Turbine oils are also preferably treated at the lower temperature.

Medicinal oils, as a rule, are precooled to about 60° F. before the addition of successive batches of acid.¹³¹

In the production of "water-soluble," or miscible, oils, warming with a total of 100 to 200 per cent by weight of fuming acid has been patented.⁴⁰ The object is to produce large quantities of sulfonates in the oil which will supply the emulsifying properties; otherwise this property is provided by the addition of sulfonic acids or similar emulsification agents. As heat is generated by the reaction between the acid and oil, cooling of the mixture may be necessary.¹¹² The cooling has been considered desirable even in the acid refining of semi-raw products before their final fractionation.⁴¹ A common method of handling the non-viscous distillates is to pre-cool them sufficiently so that the heat generated from contact with the acid will not heat them above the maximum permissible treating temperature.

The heat of the reaction between the acid and the oil is an appreciable factor. Thus a certain sample of kerosene, when mixed with 10 to 15 per cent by weight of fuming sulfuric acid, liberated 120 to 140 B.t.u. per pound of acid. Slightly more heat per unit of acid is given off with smaller quantities of acid and at higher treating temperatures. In the treatment of lubricating oils with acid, it was observed²²² that within certain limits the heat of reaction is directly proportional to the oil lost to the acid as sludge and that for any given oil loss, the heat of reaction is practically equal for all concentrations of acid (acids of 75 to 98 per cent concentration were investigated). The heat given off per pound of acid is much higher with unsaturated oils, such as cracked products.

Wax may be treated in a melted condition,²⁴⁹ or the oil bearing the wax may be treated before the wax is separated. The latter procedure is not so efficient in treating the wax but is usually more easily accomplished in the refinery. If wax is treated with acid, it is preferable to treat it after and not before it is sweated, in order to minimize the acid required. Otherwise the acid is partly expended in treating the oil associated with the wax.

The refining of cracked distillates is a special problem. The main object in refining some of them, especially the California, Mexican, and some other cracked gasolines, is the removal of sulfur and gum without removing the olefins and aromatics. This can best be effected with strong sulfuric acid at low temperatures; and if five pounds or more of acid per barrel is used, refrigeration can usually be economically employed. Each particular distillate has its own characteristics, and these must be determined experimentally in the laboratory or otherwise.

It is often impossible without refrigeration to reduce the sulfur to the desired amount by simply increasing the quantity and concentration of the acid. Robinson¹⁹⁹ showed that strong sulfuric acid, especially fuming acid, removed sulfur from kerosene stock more efficiently if the stock was first cooled to 38° F. than if the stock was at normal temperatures. Thus kerosene with 0.05 per cent sulfur content was obtained by using either 20 pounds of 98 per cent acid per barrel at 38° F., or 25 pounds at 44° F., or 37 pounds at 50° F., or 44 pounds at 56° F. Robinson reported that by cooling the kerosene to about 38° F., he could reduce the sulfur with 40 per cent less acid than required at normal temperature. The cold treatment was unsatisfactory, however, for stock containing constituents which cause the kerosene to smoke. For that reason the cold-treating process had a very limited use.

Much later the advent of cracked gasoline introduced an entirely different refining problem from that which had been known before. At present the only practical commercial method of removing the sulfur from the cracked gasoline without seriously affecting the knock rating or polymerizing the valuable olefins and removing the aromatics consists in maintaining the cracked oil at a low temperature during the acid treatment.

For treating cracked gasoline with strong sulfuric acid in large or relatively large quantities, the temperature of the cracked gasoline is not permitted to rise above about 25 or 30° F. as a maximum,¹³⁷ though in some cases a temperature of 40 to 45° F. may be found more economical. If the oil is to be treated at 25 to 30° F. as a maximum temperature, the stock must be previously cooled, so that the heat of reaction with the acid will not bring the mixture above this temperature. The cooling is likely to be as low as 5° F. for moderate amounts of acid; but if larger amounts of acid are used, the best procedure is to cool the stock first and apply the acid in increments and extract the heat between the additions of acid, as described later under the "Stratcold" cold-treating process. The oil entering the system must be dry, the drying cost being decreased by first contacting the oil with spent acid. This method of drying is not always possible, especially with cracked distillates, as some of the colored substances dissolved by the acid may be redissolved in the wet oil and the decolorization of the oil rendered more difficult. In any case the acid sludge should always be used while it is fresh, a simple operation in continuous countercurrent units.

Lower temperatures greatly decrease the polymerization losses.¹³⁷ Refiners commonly find it economical to use the cold treatment for cracked naphtha, even though they use only a few pounds of acid per barrel, because of preventing polymerization and lowering the octane rating of the gasoline. Treatment of cracked gasoline with sulfuric acid at low temperature does not remove the aromatics or polymerize nearly so much of the valuable olefins to the less valuable products with boiling points above the upper limit for gasoline, as shown in Tables 16, 17, and 18. For example, in the treatment with 20 pounds of 93 per cent acid per barrel, the excess loss of gasoline by the normal process over the cold process because of polymerization alone is about 5 per cent, and is greater for larger amounts of acid and for stronger acid. The oil treated at the low temperature is more nearly free from sulfur dioxide and other acid products. The sludge produced is more fluid than that obtained at higher temperatures.

Davis and Hampton⁹⁸ obtain best results in refining cracked naphtha by controlling the temperature of the oil during the acid treatment so that it does not rise above a maximum of about 40° F., special emphasis being given to preventing loss of the unsaturated hydrocarbons. Davis, Hampton, and Klemgard⁹⁹ precool the naphtha to a low temperature and treat it with concentrated or fuming acid under conditions favorable for sulfur removal and avoidance of polymerization losses:

Refrigeration systems used at the refineries for cold acid treatment are described elsewhere.¹³² Various patents relating to the low-temperature treatment of oils have been issued.²¹³

The data of the following four tables were developed in the research laboratory of the Union Oil Company of California in 1928 by Stagner and Dunham in an investigation of the reduction of the sulfur content of cracked gasoline at different temperatures and with acid of various concentrations. The data are published here with the consent of the Union Oil Company.

In these experiments the cracked naphtha was treated with acid and neutralized with caustic soda solution. The neutral naphtha was then tested for the amount of gasoline distilling below 400° F., as reported in one of the following tables, and some of it was subjected to steam distillation, and 90 per cent of the still charge distilled. The percentage sulfur figures pertain to the 90 per cent steam-distilled fractions unless otherwise indicated.

Table 16. Gasoline, Containing 0.39 Per Cent Sulfur, Produced from the Cracking of Gas Oil in Cross Units, Acid Treated, 90 Per Cent Steam-Distilled.*

Strength of Acid % H ₂ SO ₄	Treating Temperature (° F.)		H ₂ SO ₄ Net (lb./bbl.)	Loss to Sludge (%)	Engler Dist. of Neutral Oil to 400° F. (%)	Steam Distillate Sulfur (%)
	Init.	Max.				
103	88	98	10	5.2	90.5	0.26
103	80	98	20	6.7	88.0	0.19
103	86	102	30	10.0	...	0.16
103	80	104	40	12.0	...	0.14
103	74	106	60	16.0	80.3	0.10
103	7	20	10	5.2	92.0	0.32
103	2	20	15	6.0	91.5	0.17
103	7	23	20	9.0	88.0	0.10
103	2	25	30	10.4	87.0	0.06
93	93	102	10	4.2	91.5	0.25
93	84	97	20	5.8	88.5	0.21
93	78	96	30	8.3	...	0.16
93	76	101	40	13.3	...	0.14
93	84	102	60	16.7	81.5	0.10
93	10	16	10	4.2	93.5	0.34
93	8	18	20	5.8	92.5	0.25
93	5	20	30	10.0	91.0	0.12
93	0	21	40	10.8	90.0	0.07
93	5	28	60	15.8	...	0.04

* Courtesy, Union Oil Company of California.

In Table 16 the 90 per cent steam-distilled fractions were all 30 color Saybolt or lighter. This stock, when treated at normal temperatures in the batch method of the laboratory with a comparatively small amount, *e.g.*, 10 pounds, of 93 per cent or of fuming acid (103 per cent), gave lower sulfur content in the redistilled product than when treated at low temperatures. Curves made from these data would show more efficient sulfur reduction at normal temperatures up to the use of 12 pounds of

fuming acid or 24 pounds of 93 per cent acid per barrel. Beyond these respective amounts, the acids functioned far more efficiently at low temperatures for the sulfur removal. As a general rule, however, the aid of the cooling is manifested in the laboratory experiments with lower quantities of 93 per cent sulfuric acid than is indicated here. In Table 17, in which 20 pounds of 93 per cent acid is used on a different stock, the sulfur is reduced more at lower than at normal or elevated temperatures. However, in all cases the low-temperature treatment gave higher yields of gasoline boiling below 400° F. because of less polymerization. Octane ratings of these samples of gasoline were not made, but the cold-treating process preserves the antiknock properties of the gasoline, as shown by Graves on page 92.

Table 17. 20-Pound 93 Per Cent Acid Treatment at Varying Temperature.*
Stocks Produced from Diesol in Cross Cracking Units.
(Sulfur, 0.30 per cent.)

Temperature (° F.)		Color	Sulfur (%)	Sludge Loss (%)
Initial	Maximum			
9	25	30	0.095	5.9
10	57	30+	0.09	4.2
30	64	30+	0.10	5.0
40	60	30	0.09	5.0
50	77	30+	0.10	5.0
60	88	30	0.13	5.4
70	97	30	0.13	4.2
80	97	30	0.14	4.6
90	110	30	0.16	4.2
110	130	27	0.15	4.2
138	153	28	0.14	..

* Courtesy, Union Oil Company of California.

The stock of Table 16 was abnormal in being as amenable at normal temperatures to sulfur reduction with 93 per cent acid as with fuming acid, a condition most probably due to the fact that fuming sulfuric acid at normal temperatures attacks the unstable hydrocarbons and adds its own sulfur to the oil. At lower temperatures the fuming acid was much superior to the 93 per cent acid for desulfurization. In Table 16, 20 pounds of fuming sulfuric acid at a low temperature reduced the sulfur to 0.10 per cent; but to reduce the sulfur to this figure at normal temperature, 60 pounds of the fuming acid was required. This disparity is greater than usual, although no practicable amounts of acid of any concentration at normal temperature will reduce the sulfur of some stocks to this figure. Moreover, in gasolines cracked from heavy stock the desulfurization in the treatment at normal temperature may be very slight with increases in the amount of acid; or in somewhat rare cases the sulfur content may actually increase very markedly within limits with greater amounts of acid until a maximum is reached, and then the sulfur content

decreases with still more acid. Table 18 illustrates this effect. The data of this table are taken from a curve in which the number of pounds of fuming acid used was plotted against the sulfur content in the 90 per cent fraction steam-distilled from the neutral oil. Treatment with 93 per cent acid gave an identical curve, although 50 per cent more acid was required to give the same desulfurization.

Table 18. Cracked Gasoline from Heavy Gas Oil. Anomalous Behavior in Refining at Normal Temperatures.*

(Sulfur in Raw Gasoline, 1.12 Per Cent.)

103% Acid (lb./bbl.)	Sludge Loss (%)	90% Steam-Distilled Fraction Sulfur (%)
10	4	0.34
15	5.5	0.23
20	6.5	0.18
25	7.5	0.20
30	9.0	0.25
35	11.0	0.27
40	13.0	0.25
50	16.0	0.23
60	19.0	0.19
70	22.0	0.11
80	24.0	0.07

* Courtesy, Union Oil Company of California.

In Table 18 it will be noticed that 20 pounds of fuming acid reduced the sulfur to 0.18 per cent; but from this 20 pounds up to 35 pounds, the content of sulfur in the gasoline increased, and 60 pounds was required to give 0.19 per cent sulfur, or approximately the same percentage as produced by 20 pounds. The loss to sludge was approximately a straight-line function of the amount of acid used, although a limit would have been reached with still more acid, at which the loss to sludge per pound of acid would decrease because of the elimination of the more reactive constituents of the gasoline.

The selective removal of the sulfur compounds, especially at low temperatures, is perhaps mainly a solvent process, although there is the possibility of forming loose combinations between the sulfuric acid and the sulfur compounds. Strong sulfuric acid is known to be a good solvent for certain organic compounds; for example, benzophenone ($\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$), in many ways a reactive chemical, is very soluble in concentrated sulfuric acid; in fact, a method of increasing its purity consists in dissolving it in concentrated sulfuric acid, discarding the constituents not dissolved, and precipitating the pure benzophenone from the acid by pouring the acid solution into a large volume of water. The benzophenone is not soluble in dilute sulfuric acid.

In the treatment of the cracked gasoline at normal temperatures, sulfur

dioxide is evolved, a reaction which shows that oxidation is in progress, but at low temperatures practically no sulfur dioxide is formed. The chemistry involved in the rise in the sulfur content in the redistilled gasoline, as illustrated in Table 18, is obscure. Alkyl sulfides can be oxidized to volatile sulfones, but not readily. Sulfur dioxide can react with certain olefins and form sulfones. Cyclopentene, pure or in cracked gasoline, reacts with sulfur dioxide to give a solid sulfone.¹⁹² Mercaptans can be oxidized to alkyl sulfonic acids, which are extremely stable to heat or to heat and acid or alkali solutions. Whether alkyl sulfonic acids and esters could be formed from the sulfuric acid and complex hydrocarbons in the cracked stock, under the influence of the stock as a solvent at normal temperatures, seems doubtful.

The stability of alkyl sulfonic acids from methyl to hexyl, inclusive, to heat and to the hydrolytic effect of aqueous alkali solutions has been examined.²⁵⁰ The stability was found to increase with the increase in the size of the alkyl group from ethyl to hexyl. The *n*-hexyl sulfonic acid ($C_6H_{13}\cdot SO_3H$) was heated in caustic soda solution of approximately 15 per cent strength for three hours at 650° F., and only 13.3 per cent of it underwent decomposition in that time. Apparently no measurements have been made of the volatility of the alkyl sulfonic acids in hydrocarbons and steam at about 250° F.

In this connection an interesting experiment was made in the Union Oil Company laboratory. A sample of cracked gasoline was agitated with acid at normal temperature, and the whole mixture quickly cooled and further agitated. When the gasoline was then finished in the usual way, its sulfur content corresponded to that of normal-temperature treatment rather than to low-temperature treatment. This behavior indicated that products containing sulfur had been formed at the normal temperature, which the acid could not extract at the lower temperature.

Many of these phenomena remain unexplained, as does the fact that in the batch, or one-stage, laboratory treatment smaller amounts of acid up to about 10 pounds may remove more sulfur at normal than at low temperature, whereas larger amounts of acid extract more at low temperature, although the polymerization losses are far greater at normal temperature than at low temperature.

A tabulation (Table 19) is presented to show the effects on polymerization of treating a cracked gasoline with acid at various temperatures. The gasoline was produced from a light California gas oil and contained about 0.40 per cent sulfur. The Engler distillations were made on the "neutral" oil before the oil was steam-distilled.

The data of Table 19 show the increase in the boiling range of the cracked gasoline when refined at normal temperatures over that refined with like amounts of acid at low temperatures. This effect is due to the greater polymerization of the olefins at normal than at low temperatures.

The boiling points when 90 per cent of the respective samples had been volatilized (the 90 per cent point) offer instructive comparisons. Table 16 also shows the greater polymerization effects of the acid at normal than at low temperatures. In the next to the last column of that table is shown the percentage distilled at 400° F. The loss of olefins through

Table 19. Engler Distillation Data on Acid-Treated Cracked Gasoline.*

Temp. (°F.)	Treating Conditions		Temperatures in Engler Distillations													Max.	%
	Acid Used (%)	(lb./bbl.)	Init.	10%	20%	30%	40%	50%	60%	70%	80%	90%	95%				
Stock		0	83	150	195	234	268	295	323	353	377	404		418	94.5		
100	103	10	116	166	208	244	276	304	329	355	379	402	425	478	98		
100		20	110	166	220	255	286	310	336	360	383	419	446	470	97		
100		60	104	184	236	274	304	330	352	374	402	444	540	600	98		
20		10	94	158	204	238	268	294	316	344	370	396	410	438	98.5		
20		15	96	160	204	240	272	298	324	344	372	396	414	442	99		
20		20	96	164	214	250	280	308	330	358	386	406	436	448	98		
20		30	108	172	220	260	286	312	336	359	380	410	450	470	99		
100	93	10	100	166	210	244	276	302	324	348	374	398	414	460	99		
100		20	104	176	222	260	290	314	336	358	380	408	440	506	98		
100		60	104	182	232	270	302	326	348	372	398	432	500	576	98		
20		10	97	156	198	234	265	292	316	340	364	389	406	427	99		
20		20	94	158	208	240	272	297	320	345	370	394	406	432	99		
20		30	89	160	206	244	275	300	322	347	370	396	416	440	99		
20		40	96	166	214	252	286	308	329	346	378	401	424	478	99		

* Courtesy, Union Oil Company of California.

polymerization by acid to di-polymers boiling beyond the range of gasoline is one of the most serious problems in refining cracked gasoline, especially when the sulfur content is high and must be reduced.

The low-temperature treatment of cracked naphtha was first used commercially by the Standard Oil Company of California, but now it is in extensive use by other refineries. This process in its original installation has been described as follows:*

"The cold-treating process for cracked naphthas, developed and patented by the Standard Oil Company of California, is based on the theory that strong sulfuric acid retains its activity as a solvent for sulfur compounds at all temperatures but is not such an active polymerizing nor sulfonating agent at low temperatures. Cold treatment has not only resulted in a substantial reduction in treating losses but has also reduced the quantity of sulfuric acid required for any desired reduction in sulfur content. The following table is indicative of the savings in acid and in gasoline accomplished by cold treatment:

Acid required for normal treatment (without cooling)			
(Pounds 98% acid/barrel of cracked naphtha)	8.4	21.0	42.0
% Increase in gasoline yield by cold treatment	5.9	16.8	37.0
% Decrease in acid required by cold treatment	20.0	41.6	56.1

* Communication from R. A. Halloran, Manager of Research and Development Department of the Standard Oil Company of California.

"The following data are indicative of the beneficial effect of cold treatment in the preservation of antiknock properties:

Acid required for normal treatment (without cooling) (Pounds 98% acid/barrel of cracked naphtha)	8.4	14.7	21.0
Additional drop in octane number of finished gasoline by normal treatment as compared to cold treatment	7.5	11.5	14.0

"A flow diagram of a commercial installation of the cold-treating process is attached. The two-step counterflow principle of acid application is employed, and temperatures are maintained at about 20° F. Untreated naphtha is fed from storage to a water separator to remove entrained water and is passed through a series of coolers where the temperature is reduced to 0° to 10° F. The naphtha is then mixed with once-used acid sludge in a centrifugal mixing pump, the temperature of the mixture discharged from the pump being maintained at 20° F.

"This mixture is passed to a settler, the naphtha from which is led to a second series of coolers. The sludge from this settler is taken to a second settling unit where recovered naphtha is separated and returned to the plant feed; sludge from this settler is sent to an acid recovery plant.

"The naphtha is cooled to 10° to 15° F., fresh acid added, and mixing carried out in two centrifugal mixing pumps with cooling between, so that the temperature out of each pump is maintained at 20° F. The last mixing pump discharges into another settler, the sludge from this unit going back to treat fresh naphtha, and the naphtha passing to a horizontal drum for final removal of traces of sludge. The acid naphtha leaving this vessel is finally washed with water and caustic treated by conventional means before passing to treated naphtha storage.

"The refrigeration for the plant is accomplished by direct expansion of ammonia. Liquid ammonia from storage is fed into accumulators and thence to coolers, each accumulator feeding several coolers. From the coolers the gaseous ammonia is led back to compressors, then through condensers and back to storage, thus completing the cycle. Economy in refrigeration is obtained by complete insulation of lines, coolers and accumulators, and by cold exchangers where possible. Refrigeration requirements are approximately 100 tons per 1000 barrels of cracked naphtha treated daily. The cost of refrigeration is comparatively small, amounting to less than 0.1 cent per gallon of naphtha treated.

"In addition to the increased gasoline yield and quality and the reduced acid requirements, the cold-treating process has the following advantages:

- (a) Decreased caustic soda requirements (50 to 60 per cent decrease) for the neutralizing and subsequent distillation steps.
- (b) Less emulsion trouble in the water washing and caustic soda

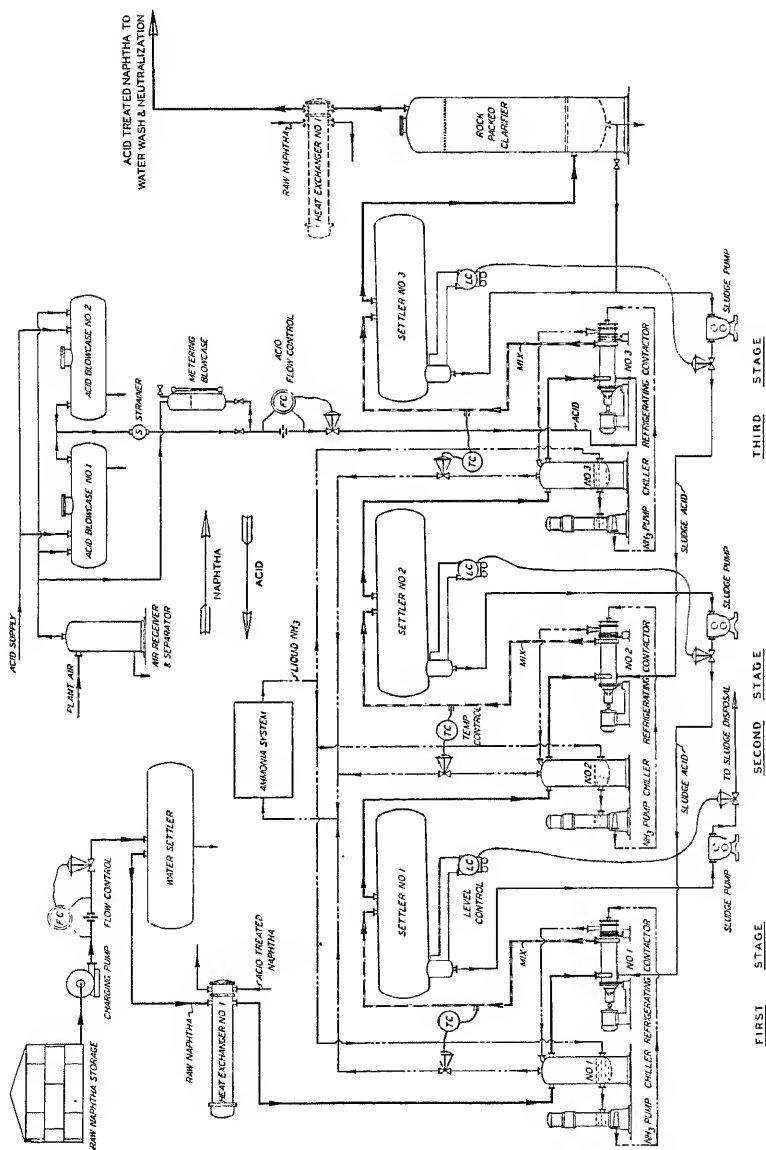


FIGURE 3. Cold Treatment of Cracked Naphtha.
 Courtesy, Standard Oil Co. of California.

washing steps following the acid treatment, thereby giving increased capacity and lowered processing costs in a continuous treating plant.

(c) Less gum-forming constituents in the finished gasoline, thereby making the process applicable also to naphthas from vapor phase cracking, where gum reduction is particularly necessary.

(d) Improved color stability of the finished gasoline.

(e) Improved yields of acid where spent acid recovery is practiced, thus resulting in decreased acid costs."

Halloran¹¹¹ presented the following data shown in Table 20 on the use of 98 per cent acid at different temperatures to produce a gasoline of 0.15 per cent sulfur from cracked naphtha containing 0.71 per cent sulfur. The temperatures shown are the highest attained in the oil and acid mixture during the treatment.

Table 20. Treatment of California Cracked Naphtha at Various Temperatures to Produce Gasoline of U.S.M.G. Boiling Points Containing 0.15% Sulfur

	Gravity of Naphtha % Sulfur % Gasoline (U.S.M.G.)		53.7° A.P.I. 0.71 93.0				
Maximum Temperature of Treatment (°F.)	5°	20°	30°	45°	60°	100°	166° *
Lbs. of 98% Acid per Gal. of Naphtha	0.60	0.51	0.60	0.63	0.84	1.15	1.50
% Sulfur in Treated Naphtha	0.27	0.38	0.36	0.49	0.58	0.74	0.79
% Gasoline in Treated Naphtha	88.7	90.5	86.6	84.1	79.8	74.0	62.2
Polymerization Loss†	4.6	2.7	6.9	9.6	14.2	20.5	33.1
Acid-treating Yield	92.7	92.7	92.8	91.8	90.2	88.3	78.9
Rerun Yield	88.7	90.5	86.6	84.1	79.8	74.0	62.2
Net Gasoline Yield from Cracked Naphtha	82.3	83.9	80.3	77.2	72.0	65.3	49.1

* Normal treatment—acid added at atmospheric temperature.

† % of original crude gasoline content lost by polymerization.

The cold acid treating process has recently undergone developments which consist essentially in equipment to provide rapid and thorough dispersion and homogeneous mixing of the acid and the cracked distillate by mechanical means, followed by quick separation of the acid sludge. The process, known as the Stratcold Acid-Treating Process, is a combination of the Cold Treatment Process developed by Halloran and collaborators with the Contactor-Centrifuge Process developed by Stratford.²²⁶ In order to insure maximum efficiency two or, more usually, three acid and acid-sludge contacting stages are employed. As the heat is continuously absorbed during the treatment, the precooling to the very low temperature formerly necessary is avoided, thus decreasing the refrigeration cost. As

an alternative, the plant is built of Settler-Centrifuge design, which provides apparatus for separating the acid sludge from the oil by settling in the intermediate stages and by centrifuging in the final stage, or even by using settling equipment in the final stage also.

The concentration of the sulfuric acid most commonly used is 98 per cent, and the optimum period of contact between the acid and oil is infinitely short, provided that the acid is dispersed in the oil to an infinitely fine degree. Comparison of single-stage laboratory treatments with the three-stage countercurrent plant treatments indicates that only about 50 per cent as much acid is required in the plant as in the laboratory to duplicate the results of the laboratory, and thus care is required to correlate properly the laboratory and refinery data in the cold-treating operations.

The following data show the advantage of the multiple-stage treatment (re-use of the acid in a countercurrent effect). If the efficiency of acid utilization in one-stage treatment is taken as unity, then by employing two stages the efficiency is raised to about 1.65, and by employing three stages to about 1.8. A greater number of stages increases the efficiency only slightly. These figures vary somewhat with the nature of the distillate.

For details of the Stratcold Process in large-scale operations the reader is referred to the descriptions of the following three installations near Los Angeles, California:

(1) The Wilshire Oil Company.²³⁰ A 6000-barrel, three-stage contactor-centrifuge unit; refrigeration by ammonia; sludge removed by centrifuges in each of the three stages.

(2) The Texas Company.⁶ 5800-barrel capacity; 3 stages; settlers instead of centrifuges to remove the sludge; designed for use of 98 per cent acid, but a pre-wash with weak sulfuric acid (35 per cent) is made to remove nitrogenous compounds.

(3) Richfield Oil Corporation.⁷ 11,000-barrel capacity; three-stage, countercurrent; settlers instead of centrifuges to remove the sludge, and separation of the last traces of sludge by means of a clarifier consisting of a tower packed with graduated sand and gravel.

Low-Temperature Treatment and Octane Rating

Graves,¹⁰² of the Standard Oil Company of California, has recently made an extensive study of the acid refining of gasoline with special reference to its effect on the knock rating and a study of the effect of the

Table 21. Effect of Acid Treating Temperature on Knock Rating of 400° F. End-Point Cracked Gasoline.

Treating Temp. (°F.)	None		Lb. of 98% Acid per Barrel of Raw Naphtha ^a		21.0		31.5	
	Octane No.	Sulfur, %	Octane No.	Sulfur, %	Octane No.	Sulfur, %	Octane No.	Sulfur, %
20	69.8	0.54	68.5	0.34	67.3	0.13	65.7	0.06
70 ^b	69.8	0.54	67.0	0.28	65.1	0.215	62.7	0.14

^a Raw naphtha cracked commercially from a mixed California residuum.

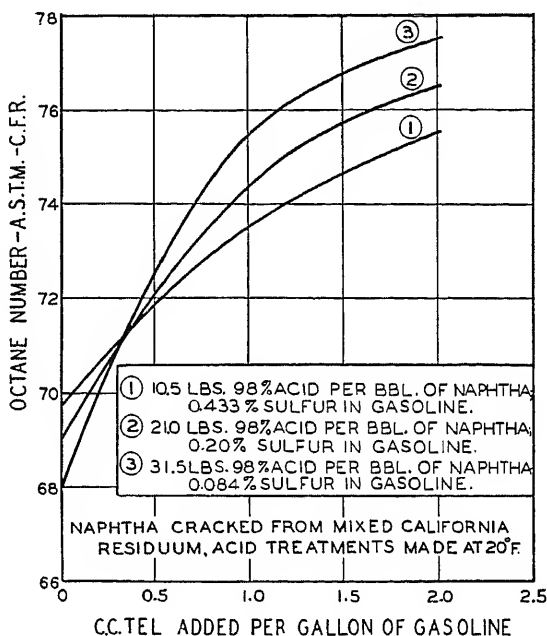
^b Initial with no subsequent control.

sulfur content of the gasoline on lead susceptibility, or efficiency of tetraethyl lead in increasing the octane number.

Many tables and graphs are given in the original publication. Only two of the tables and two of the graphs are presented here. Table 21 shows the comparative effects on knock rating and on sulfur reduction of treating a cracked gasoline with varying amounts of 98 per cent acid at normal and at low temperature (20° F.).

FIGURE 4.

Effect of Acid Treatment on Knock Rating and Tetraethyl lead Requirements of a 400° F. End-point California Cracked Gasoline.



However, offsetting the drop in the knock rating of the gasoline due to the acid treatment is the rise in the lead susceptibility of the treated gasoline as the sulfur is removed, as shown in Figure 4 in the curves plotted by Graves.

If tetraethyl lead is not used, the sulfur in the gasoline does not seem to affect the octane value of the gasoline, but it does seriously inhibit the action of the tetraethyl lead when the latter is added. Also the poisonous effect of the sulfur on the tetraethyl lead is influenced by the nature of the gasoline; its effect is most deleterious in aromatic gasoline, least in straight-run gasoline, and intermediate in the normal cracked gasolines. Figure 5 from Graves' paper illustrates this behavior.

Typical results of the effect of acid treatment on the knock rating and lead susceptibility of cracked gasoline are given in Table 22.

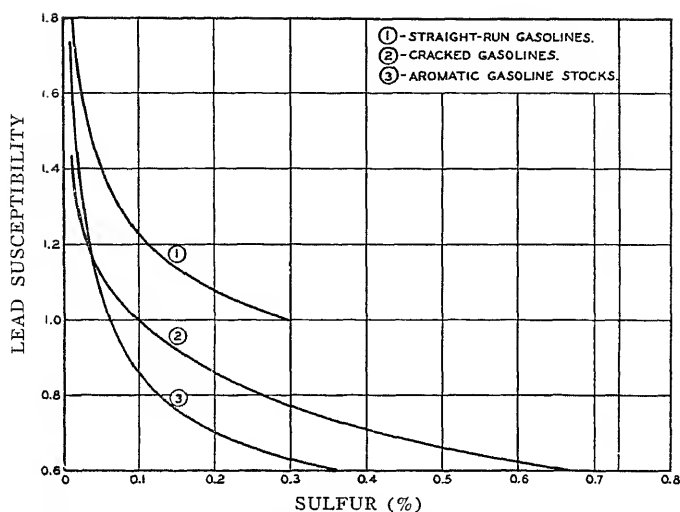


FIGURE 5. Relation between Lead Susceptibility and Sulfur Content for Different Gasoline Stocks.

Table 22. Comparative Effect of Acid Treatment and Sulfur Content on Lead Susceptibility of Cracked Gasoline.

Acid rate, ^a lb./bbl. of raw naphtha ^b	10.5	21.0		31.5		
A. S. T. M. boiling range, °F.:						
Initial	110	104		100		
End point	406	390		396		
Sulfur content, %:	A ^c	A ^c B ^d		A ^c	C ^e	B ^d
Total	0.433	0.20	0.44	0.084	0.20	0.42
Disulfide	0.013	0.004	0.013	0.001	0.004	0.013
Sulfide	0.025	0.006	0.025	0.004	0.006	0.025
Residual (thiophene)	0.395	0.190	0.395	0.079	0.190	0.395
Octane No. with following cc. of tetraethyl lead per gal.:						
0	69.7	69.0	69.0	68.0	68.0	68.0
0.5	71.5	72.0	71.0+	72.5	71.0	70.0+
1.0	73.5	74.5	73.0	75.5	73.5	72.0
2.0	75.5	76.5	75.0	77.5	75.5	74.5
Lead susceptibility	0.63	0.79	0.61	1.02	0.80	0.69

^a 98 per cent sulfuric acid treating at 20° F.

^b Naphtha cracked from mixed California residuum.

^c Gasoline as produced.

^d *N*-Amyldisulfide, propyl sulfide, and dimethyl thiophene added to equal total sulfur content and amounts of the different types of sulfur compounds in gasoline from 10.5-pound treat.

^e Same as ^d except to duplicate 21.0-pound treat.

Time of Contact

The time of contact of acid and oil is usually of great importance. Unduly prolonged reaction time may impair the color or stability of color of the oil and is almost sure to increase the content of neutral sulfuric

esters, whereas the quick removal of the acid from the oil, especially a heavier oil, may prevent efficient utilization of the acid. For the removal of sulfur compounds from the oil, better results may follow if the time of contact is longer than is required for betterment of color. However, the optimum time of contact is dependent upon the degree of dispersion of the acid, or intimacy of contact of acid and oil, and should be tested experimentally for the type of agitation and for the kind of oil being refined.

The time during which the oil is in the acid state can be divided into three distinct stages:

- (1) Time of agitation to effect thorough contact.
- (2) Time of settling the sludge.
- (3) Time which elapses after the sludge is withdrawn and before the oil is neutralized. This last period is of relatively less importance than the preceding two, as the oil can be kept in the acid state, but not in contact with the sludge, for a rather long time without serious results.

Thus a sample of straight-run western kerosene stock was kept in the acid state for several days without any undesirable effect on the color. Likewise, as noted previously, some of the Mid-Continent lubricating oil stocks have been kept in the acid condition for 48 hours at temperatures close to 200° F. without deterioration.

The length of time required for agitating the oil with the acid depends on:

- (1) Method and violence of agitation.
- (2) Size and shape of the apparatus.
- (3) Viscosity of the oil at the treating temperature.
- (4) Quantity of acid.
- (5) Strength of acid, as stronger acid requires less time.
- (6) Number of fractions in which the acid is applied.

Kerosene stock, when treated with a large amount of acid for improvement in burning qualities, is agitated by means of air, the time usually being from 30 to 40 minutes. Gasoline, both straight-run and cracked, is treated in continuous processes, and the actual time of agitation is usually only a few seconds.

The acid treatment of lubricating oils in 25- to 1200-barrel agitators requires at least 30 minutes' agitation, and under ordinary conditions complete mixing is attained in less than two hours, one hour being the usual time of agitation in commercial practice.^{4, 247} About the same time of agitation is used in treating transformer oils. For the last fraction of acid added to the oil, more time is often given than for the first fractions. Laboratory tests show the time required for best effects, as well as for best

utilization of the acid. Weir, Houghton, and Majewski²⁵³ have presented excellent data on laboratory control and treatment of lubricating oils.

In the production of "water-soluble" or emulsifiable hydrocarbon oils, long contact with the acid sludge has been claimed to be beneficial. Thus, in one process the oils are treated at high temperatures (about 230° F.) with acid containing free sulfur trioxide.⁴⁶ The indicated weight of acid is about twice that of the oil. The treated oil is then kept in contact with the sludge until the oil has the desired properties.

Needlessly prolonged agitation is usually harmful, as pointed out above, because part of the sludge undergoes chemical change and the tarry material redissolves and discolors the oil. Long agitation of lubricating oils with the acid may give the oil a greater tendency to emulsify when the alkali is added for the neutralization. Air has a tendency to oxidize the oil to organic acids, which form soaps with the alkali solution. Excessive sulfonation also takes place. It should be pointed out that the actual time of mixing does not include the time of settling the sludge from the oil because during settling the interphase between the acid and oil remains practically unchanged.

Sulfuric acid forms with resinous substances certain extremely labile compounds, which are immediately decomposed by cold water.¹⁰⁷ Moreover, the continued oxidizing action of the acid on the sludge in contact with the oil may release deleterious substances in the oil.

With cracked distillates quick, intimate contact of acid and oil and quick separation of the sludge are of special importance, particularly if stability of color is desired, even though longer contact may give a slightly greater removal of sulfur compounds, perhaps through a better conversion of the alkyl sulfates to acid alkyl sulfates, which are then soluble in the acid.

The time of contact of the acid with cracked gasoline is preferably limited to a fraction of a minute so as to avoid as much as possible polymerization and sulfonation of the oil. In the treatment of cracked gasoline a prolonged period of contact with the acid sludge also causes a large increase in the quantity of sulfur dioxide formed during the subsequent steam distillation and, therefore, exaggerates the corrosion difficulties.

Time of contact for cracked products is limited in some patents to half a minute or less.⁵² Walton²⁵¹ finds that the optimum time of contact may vary from 30 to 60 seconds and that in modern contactors the time may be reduced to a minimum of 10 to 20 seconds. In treating cracked distillate at the refinery of the Louisiana Refining Corporation the best results were obtained when the time of contact in their plant equipment varied between three and five minutes. With a longer time of contact, the sulfur content could be further reduced, but the color was impaired and more acid (sulfur dioxide) was formed in the re-run stills. A storage of the gasoline for a day or more after it was treated but before it was redistilled had no effect on the content of sulfur but improved the color of the finished product.¹⁹¹

An extended study of the optimum time of contact of acid with cracked gasoline has recently been made by Sager.²⁰⁴ He found that less than 60 seconds' time of

contact with concentrated sulfuric acid was sufficient to attain the maximum of sulfur removal from Iraq, Iranian, and Venezuelan cracked distillates. The gum stability was increased by longer time of contact, but so also were the polymerization losses and the total operating costs. The addition of an inhibitor gave satisfactory gum stability to the finished product. He used as inhibitor the natural phenols (primarily *p*-cresol) extracted from cracked distillate before the acid treatment.²⁰³

The Iraq cracked distillate contained 0.34 per cent sulfur and when treated with about 6 pounds 96 per cent acid per barrel at temperatures varying from 50 to 70° F., had practically as good color and actual gum content after 34 seconds' contact with the acid as after 124 seconds' contact; the longer contact reduced the sulfur content only 0.003 per cent (0.168 per cent sulfur at 34 seconds, and 0.165 per cent sulfur at 64, 94, and 124 seconds).

Similar treatment of the Iranian cracked distillate showed that the maximum sulfur reduction had occurred at the end of the first ten seconds of contact. Longer contact increased the polymerization loss but decreased the potential gum. The addition of a little of the natural inhibitor noted above gave the product from the ten seconds' contact as great gum stability as that from a contact time of 120 seconds without the inhibitor. The Venezuelan naphtha gave similar results.

The separation of the sludge from the oil can be effected either by direct settling or by accelerated methods. In treating heavy lubricating oils, the sludge should be withdrawn from the agitator during the settling period before it has time to solidify. If this is not done, the color of the oil and some of its other properties may be impaired because the sludge begins to "work," *i.e.*, to decompose, as evidenced by the formation of gas bubbles on the surface of the oil and evolution of sulfur dioxide. The time during which the sludge may be left in contact with the oil depends on the nature of the oil and the treating temperature. However, the sooner the sludge is withdrawn, the less the danger of injury to the oil. In some refineries the removal of the sludge is begun almost as soon as the agitation is stopped. The first fraction is withdrawn after as little as five or ten minutes of settling, the second after 30 to 60 minutes, and, if almost all of the sludge has then been removed, the oil is left overnight for the final traces to settle out.

The time of settling is different for different distillates and may vary from a few seconds in gasoline to 12 hours or more in viscous oils. If the acid is applied in several additions, less settling time is allowed between the successive portions of acid than after the final portion. Under these conditions, settling of one-half to two hours is frequently adequate. At higher temperature the viscosity of the oil is less, and this low viscosity greatly increases the settling rate. Complete separation of the sludge from heavy oils is always important to facilitate further operation.

If contact treatment (dry neutralization) with clays unactivated with acid follows the acid treatment of light oils, a small amount of acid in the oil may be beneficial in activating the clay. However, in treating lubricating oils, best results seem to be obtained when the acidity of the treated oil is reduced to a minimum.

Table 23. Acidity of Lamp Oil after Gravity Settling for Various Lengths of Time.

Time of Settling (hours)	Cc. of 0.1 Normal NaOH Solution per 100 cc. of Oil for Neutralization
0.5	10
1.0	9
1.5	7
2.0	6.8

The decrease in acid content of one oil with settling time is illustrated in the experiments on a lamp oil distillate shown in Table 23.⁶⁴

It is impossible, however, to predict even approximately the settling rate for a given oil, as the rate varies not only with the nature of the oil but also with the degree of dispersion of the acid, type of agitators, temperature, etc., and the results obtained in the laboratory may differ greatly from those of the plant.

ACCELERATED METHODS FOR SEPARATION OF ACID SLUDGE

Accelerated methods, both mechanical and chemical, exist for the separation of the acid sludge. Among the best known mechanical methods are centrifuging, filtering, passing the mixture through a series of baffles, and percolating the mixture through sand or gravel.

Mechanical Methods

Separation by centrifugal methods³ may be accomplished either by passing the mixture of acid and oil through a centrifuge or by creating a centrifugal force by rotating this mixture in a system of pipes or within a separating tank. However, the latter method, although apparently cheaper, is not well suited for commercial practice because, unless the equipment is properly designed and operated, emulsification and not de-emulsification of the acid and oil may result. Alkali, alcohol, acetone, benzene, and similar substances may be added to the oil before centrifuging to facilitate the separation, but they are seldom, if ever, used commercially because of the additional expense, particularly as the cost of centrifuging is itself high.

Centrifugal equipment for separating acid sludge is used on light and heavy petroleum distillates and residual stocks. With light stocks, such as cracked gasoline, centrifugal separation is beneficial primarily for decreasing the time of contact between the acid and oil. The main object of the centrifuging of residual lubricating oil stocks is the reduction of the amount of oil lost in the acid sludge.

Centrifuging is expensive, and before a decision is made to install the necessary equipment, the cost and profit balance should be carefully weighed. In general, in treating gasoline for color and gum, centrifuging

gives products of equal or better quality than other methods. In the use of mechanical agitation rather than air agitation in the units involving centrifuging, poor colors may arise, not because of the centrifuging but because of the method of agitation, a condition especially true in the treatment of kerosene from certain types of crude oil. This effect of mechanical agitation is discussed later in more detail on page 282. In treating lubricating oil stocks of low viscosity, centrifuges usually yield more oil and lower acidity than the conventional methods. However, in treating residual stocks the separation of the sludge may not be so complete as in the conventional treatments, an effect which is to be ascribed not so much to the method as to the expense of centrifuging the stocks long enough for complete separation of the sludge.

The percolation of light oils containing acid sludge through sand or gravel provides a cheap and fairly efficient method of separating the sludge.^{62, 185} If only a quick separation of the main body of the acid sludge from the oil is desired, as in treating certain cracked distillates, a gravel bed alone is very satisfactory; but for a more complete separation of the sludge, a rather fine bed of sand is needed, requiring a fairly large filtering area. The time of separation with a sand filter is longer than with a gravel filter unless considerable pressure is applied. The sand and gravel filters can be of vertical or horizontal type, the latter being preferable, as the use of a settling tank after the filter can be avoided and the streams of acid and oil can be withdrawn separately from the filter. The further addition of raw clay to the acid oil removes the last traces of acid.

Acid sludge may be separated from oil by passing the acid-treated oil through solid foraminous blocks with capillary passages.⁹² Teitsworth reconditions the sand filters by hydrolyzing the sludge with water and then dissolving the hydrolyzed sludge from the sand with oil or by treating the filters with sulfuric acid.²⁰²

Osmer and Craise¹⁸⁵ use a percolation tower, or equivalent device, packed with gravel of the minimum size that will permit the separated acid sludge to flow downward against the rising gasoline. The oil and the acid sludge are initially delivered to the bottom of the column, from which they start to move in an upward direction through the gravel. As the sludge adheres to the gravel, it flows in thin films back to the bottom of the tower and permits the oil, freed of the sludge, to flow out at the top of the column in an uninterrupted manner.

A system of baffles can be used with advantage¹⁴² for the main mass of the acid sludge.

Peppery sludge can be removed from acid-treated lubricating oils by the addition of the minimum of "filter aid" to the oil and filtering.²⁰² Also dry sand, clay,¹⁹³ or other similar agents may be added to the acid oil with gentle agitation until the sludge gathers into particles or into lumps, sometimes as large as peas.

Chemical Methods

Chemical methods for accelerating the separation of the acid sludge are of special importance for the viscous oils from which the separation of the



sludge is rather difficult. It should be noted that certain oils of this type, particularly those treated with sulfuric acid following refining with solvents, present special difficulties, which have not always been overcome in commercial or even in laboratory practice.

As a general rule, water is used to hasten the separation of the sludge. The quantity of water is variable, depending on the type and viscosity of the stock. Lubricating oils of light viscosity usually require slightly less water than the more viscous oils. In general, the quantity of water is about 0.5 per cent of the volume of the oil, but it may vary from 0.25 to 2.0 per cent. With an unfamiliar stock, the water is added very carefully until the sludge particles agglomerate sufficiently. If more than the optimum of water is added, the particles lose their sharpness, and undesirable hydrolysis of the sludge occurs with partial redissolving of the tars in the oil. With too little water most of the sludge remains in the peppery condition. When water is added to the oil, only mild agitation is used, as otherwise the particles of sludge are broken into finer divisions instead of coalescing into larger divisions. A certain amount of skill is, therefore, required to coagulate sludge properly. Instead of water, a solution of an electrolyte,⁹⁶ such as sodium carbonate solution or sodium hydroxide solution of varying strengths, may be used.

The addition of one per cent of oleic acid to the acidulated oil is recommended for coagulating peppery sludge. Naphthenic acids obtained from kerosene stock before the acid treatment are sometimes added, although the naphthenic acids extracted from the kerosene after the acid treatment have less effect on the sludge.^{108, 189} The addition to cracked gasoline of about one per cent of paraldehyde, acetal, or other aldehydes, their polymers, or substances capable of yielding aldehydes, is claimed to facilitate the separation of sludge and to improve the refining power of the acid.¹⁶⁰ Vegetable or animal oils are likewise claimed to be suitable for the same purpose.¹⁸⁸ Observations have been reported that in refining a mixture of two oils with acid, the sludge may separate with greater difficulty from the blend than from either of the components treated separately.²¹¹ This condition certainly does not occur often.

After the sludge is coagulated and withdrawn from the agitators, it is common practice to wash the oil with small quantities of water before neutralizing with sodium hydroxide or clay.²⁴¹ This water washing serves to remove further quantities of acid sludge, which, if left in the oil, may hydrolyze with caustic to a much greater extent than with water. Likewise, the water is beneficial if clay is used for neutralization, for otherwise the quantity of acid left in the oil may be excessive and require very large quantities of clay. The water washing is less important in the non-viscous distillates, such as gasoline or kerosene, from which the sludge

settles rapidly. However, in many instances, the quality of even these light distillates is improved by water washing.

The removal of acid and sulfur dioxide from viscous acid-treated oils is particularly important. These viscous oils are freed of the acid and sulfur dioxide by agitation with strong currents of air with or without the addition of small quantities of water.³⁶ Lighter distillates, such as transformer oils, may be agitated with air without the addition of water, whereas the heavy distillates, such as residual stocks, may be agitated with two per cent or more of water. The air agitation is continued until the oil is freed of sulfur dioxide. The oil is then settled for several hours to permit coagulation of all the sludge.

Method of Application

The acid is commonly applied to the oil in more than one addition. This method is preferable to adding all the acid at one time for the temperature of the oil can be better controlled, and the water, which is usually present in the stock,* is removed with the first fraction of acid and thus cannot dilute the subsequent additions of acid and lessen their refining power. If the first portion of acid is small, it carries down a relatively high percentage of organic matter as acid sludge, most of which is soluble in benzene; but if more sulfuric acid is added to this same sludge, the hydrocarbon content loses its solubility in benzene. If all the acid is added to the oil in one portion, some insoluble sludge is formed, an indication that some of the acid is spending its energy on the sludge. It is, therefore, preferable to add the acid in several portions, as otherwise some of it does unnecessary work and is wasted.¹⁰⁸

The first portion of the acid added to a lubricating stock is usually small (perhaps 5 per cent of the total) and has as its primary purpose the removal of water and the most chemically reactive constituents of the oil. The sludge acid from the final additions of acid may be used economically on a fresh batch of stock. This use of the sludge is not possible for all distillates; thus, if cracked products which contain a little water are given a preliminary treatment with sludge, the color of the oil may be impaired. More than one addition of acid may be used for the complete drying of some petroleum products. For lubricating oils a settling time of from one to three hours is usually desirable after each addition of acid.

It is important to withdraw as much of the sludge as possible after each addition of acid. When fuming acid is needed, it is claimed by some

* This refers primarily to water held by the oil in suspension. The maximum amount of water actually dissolved in oil is in the range of about a half ounce per barrel of oil.

that it is advantageous first to extract the most reactive substances with 66° Bé. acid, and again use 66° Bé. acid after the fuming acid treatment to remove the color-forming and malodorous substances which are formed by the fuming acid and which would otherwise remain dissolved in the oil. Modifications of this procedure have often been used in practical operations, although there is considerable question about its merit under all circumstances.

Concentrated acid may be used before treatment with fuming acid^{21b} or a dilute acid of less than 50 per cent concentration may be used before the treatment with concentrated acid¹⁷³ in order to avoid resinification and oxidation. An acid of 75 to 100 per cent strength may be applied after treating cracked distillates with fuming acid.¹² Other types of oils may be similarly treated.^{2, 179, 225}

The methods of mixing and agitating the acid and oil together vary considerably and may roughly be classified as follows:

(1) Mechanically driven paddles are not used extensively. Water-cooled agitators may be employed with such installations.¹¹²

(2) Circulating pumps are sometimes used for light distillates.⁸⁸ Excessive treating time is required, as the mixing proceeds slowly, and the method is, in general, very unsatisfactory because of the excessively long contact time between the oil and the sludge.

(3) Air has been used for agitating all the different distillates with the exception of the very lightest fractions.¹⁶⁶ It is fairly rapid, thorough, easy to regulate, and initially cheap to install. However, the loss of light oils to evaporation is excessive, and the oil may be appreciably oxidized. Air agitation, therefore, is seldom applied at higher temperatures and to light distillates, although in some instances such oxidation when applied to lubricating oil stocks¹⁶⁵ may result in superior products. If air is used on any stock, the time of contact should be reduced to a minimum. However, the agitation of certain light stocks with air, or even with inert gases, has often been found to give better color than mechanical agitation. The cause of this difference has not been determined. Agitation with air also has the disadvantage of diluting the acid with moisture carried by the air. This fault is sometimes remedied by first passing the air through the spent acid from a previous treatment, through some other dehydrating agent, or through a water separator where the air is kept under pressure. There is considerable fire hazard in agitating light oils with air. These various difficulties can be partly overcome by re-circulating the air from closed tanks or by using neutral or flue gases.⁶⁵ Agitation with neutral gases, moreover, has a tendency to remove the air which is already dissolved in the oil. Gas-tight treating tanks are always advantageous, even with mechanical agitation.⁶¹

The evaporation losses in the air agitation of kerosene can be roughly

calculated by assuming an average loss of about 0.0022 per cent of the oil for an equal volume of the air at 50° F. The loss for a given stock is proportional to the volume of the air, temperature, and to some extent the depth of the agitator. It doubles for about each 15 to 20° F. rise in temperature.¹⁰⁸

(4) Bubble cap towers, operated in a countercurrent manner,⁴² have been used for contacting acid and oil and give fairly good results if properly designed. Some distillates would be seriously impaired in color, however, through long contact with the acid and acid sludge.

(5) Various mechanical devices tend to effect intimate contact between oil and acid, but they are almost always designed for non-viscous oils.²²⁵ In some of them the acid is atomized and blown into the oil,¹⁵¹ a small quantity of compressed air being used for that purpose.¹⁸¹ An annular stream of sulfuric acid may be brought into contact with a confined stream of lubricating oil by means of an injector nozzle device.¹⁸⁰ Mixing can be effected by impinging the acid and oil together in a treating chamber at an angle and with high pressure.⁸⁹ A light oil and the acid can be mixed effectively by passing them through orifices,⁸² or by first injecting the two streams at an angle to each other into a chamber and then forcing the mixture through one or more orifices. Acid and oil may be mixed by delivering them to the upper surface of a rotating disc.¹⁹⁰ Acid may be contacted with oil in thin films, a method which is made possible by the application of centrifugal force.¹⁹³ Other similar devices have been proposed.⁸

(6) There are also miscellaneous methods for bringing the oil into contact with acid, such as continuously supplying acid so as to coat particles of sand in a percolator or a filter column, or other material affording a large superficial area, and then filtering or percolating the oil through this medium,¹⁵⁰ preferably in a countercurrent manner. There are still other patented devices for mixing the acid and oil.¹⁴⁵ In one method of refining in the vapor phase, the vapors are passed through pumice impregnated with the acid.⁹⁴

Whenever possible, continuous treatment is used in preference to batch treatment, as it permits closer control, decreases losses of stock, distributes the power demand throughout the day, and permits economical heating or cooling if such is required. The advantages of the principles of the countercurrent treatment have long been recognized.⁹¹ This method affords as complete utilization as possible of the acid, since it corresponds to a sludge treatment in an infinite number of stages.

Although the acid and oil may be mixed by many methods, those most commonly used for gasoline consist in adding continuously a stream of sulfuric acid to a stream of gasoline and either pumping the mixture under

75 to 125 pounds pressure through a stationary mixing device or supplying it, usually at low pressure, to the suction side of a centrifugal pump, which delivers the oil at 40 to 100 pounds pressure. The blades of the centrifugal pump give fairly good agitation, but additional mixing is usually provided by passing the mixture through several orifice plates. Morrell and Bergman give excellent descriptions and details of methods and equipment suitable for effecting good contact between acid and oil and other immiscible substances.^{169, 251, 259}

Distillation after Acid Treatment

As noted in previous pages, the acid treatment of petroleum oils may or may not be followed by distillation. The distillation of light distillates, such as gasoline and kerosene, after treatment with acid and neutralization reduces the sulfur and gum content and improves the stability of color. However, the distillation adds to the treating expense and should be used only when experimental data show it to be justified.

In re-running light distillates a certain amount of bottoms or residuum must be left in the still, and for this reason it is customary to fractionate the stock during the distillation operation so that it will have a somewhat higher end boiling point than the specification product. Normally about 5 per cent bottoms is left in the still; and the distillate treated with acid is, therefore, prepared so as to contain approximately the same amount of heavy ends. Obviously the procedure varies with the refinery needs and is also dependent on the re-running equipment in use.⁴⁸ This re-running is seldom applied to straight-run gasolines, occasionally to kerosenes, but commonly to cracked gasoline.⁵⁵

In the refining of long residuum for lubricating oil, the long residuum is sometimes treated with acid and then subjected to distillation to produce distillates and residual stocks of desired viscosities. If such a method is used, the distillate and the residual stock are thus treated in one operation, and consequently the acid may not be used most economically, for no differentiation can be made in the quantities of acid actually needed for the different fractions.

Effect of Light

Light usually discolors oils in the presence of oxygen or air and increases their acidity.¹⁰⁸ Light facilitates the absorption of oxygen, and its action is more pronounced at higher temperatures. In commercial practice, however, treatment is practically always conducted out of contact with light, and this subject need not be considered further.

RESULTS OF ACID REFINING

Color

The dark color of oil is ascribed to various impurities, especially of a bituminous and asphaltic nature. Highly unsaturated hydrocarbons,²³⁰ as well as nitrogen, oxygen, or sulfur compounds,²⁰⁷ are sometimes vaguely assigned as the cause of the colors. The reversion of color in an oil on standing, after once having been decolorized, may be due to unstable, resin-forming substances, possibly of the type of indene, coumarin, fulvenes, fluorene, and their homologs, which have a marked tendency to form peroxides,⁸³ as well as to certain sulfur compounds.¹⁷⁰

Inasmuch as the color of any oil product is practically always improved by acid or other refining, the color is to a certain extent taken as a criterion of the degree of refining. As previously mentioned, however, the color of the oil does not insure the quality of the finished product and is, therefore, *per se* of little or no value to the consumer.

The stability of the good color is usually improved by increasing the severity of the treatment. Thus a cracked gasoline treated with a large quantity of acid may have an initial color equal to, but no better than, one treated with a smaller quantity of acid; but on exposure for a few minutes to the sun or on standing in storage for a week or more, the first sample will usually show less change in color than the second.

Stability of color is usually measured by exposing samples of the oil to the action of sunlight or to some artificial source of light. In connection with these tests, it should be remembered that exposing oil in closed bottles gives considerably less change in color than the common practice of exposing them in open bottles. Difficulties arise from inability to secure a uniform source of light. The daylight varies with the season of the year, time of day, and condition of the atmosphere. Artificial sources of light, such as the carbon arc, mercury vapor lamps, electric light, etc., differ from one another in spectra and also differ from daylight. Of these light sources the carbon arc appears most nearly to resemble sunlight in spectra distribution, but it is still very different when direct comparisons with sunlight are made. It is possible to adjust the above artificial sources of light to give results agreeing with those obtained in sunlight for a given distillate exposed for a certain length of time; but the results may be entirely different if the comparative exposures are made with other oils or for different lengths of time. For this reason the use of so-called day-lamps and other similar devices for determining the color stability is at best only a method of approximating what may happen in full sunshine.

Obviously the temperature at which the sample of oil is exposed to the light is of much importance. At higher temperatures the reactions are faster, a behavior which is convenient for accelerating the test. However, when the reactions proceed faster, it does not mean that all of them are accelerated equally. For example, some gasolines tend to develop a pinkish coloration when exposed to light at higher temperatures, but only normal discoloration at lower temperatures. Unfortunately, no satisfactory method for predetermining the light stability has yet been devised.

For certain types of oils, particularly for kerosenes, the stability of the color is tested by keeping the sample in the dark for a definite length of time at elevated temperatures. These tests are intended to simulate storage conditions.

Still other color stability tests involve the measurement of the change in color when an oil is brought into contact with sulfuric acid of specified strength and under specified experimental conditions. Such acid stability tests are frequently applied to highly refined oils, such as medicinal oils. This acid stability is likewise improved by acid refining.

The color of lubricating oils after the acid treatment but before neutralization is usually blue to purple, more purple when more acid is used. After neutralization, the color is green to yellow. Finished lubricating oils are, however, in nearly all cases darker than the oils immediately after the withdrawal of the final acid sludge. The darkening is probably due to the oxidation effects of the dissolved air and the air used in drying. Doubtless some discoloration arises from the redissolving of the particles of sludge not at once withdrawn after the acid treatment.¹³⁰ Complete decolorization of heavy or viscous oils with acid is possible only through the use of very large quantities of acid, and usually other refining agents must be used in addition to the acid.

In treating lubricating oils, three types of color are sometimes distinguished: the "sour oil" color, *i.e.*, the color of the oil not yet neutralized, which is determined by straight dilution of the sour oil; the "ammonia color," which is determined after the oil has been saturated with anhydrous ammonia until no further change in color results; and the color after neutralization with caustic soda and washing with water. In measuring colors by dilution, white medicinal oils, benzene, or colorless solvents for asphaltic materials should be used as diluents, as light distillates may give erroneous results.²⁵³

Fluorescence of oils is ascribed to certain compounds of aromatic character, to traces of substances of the nature of chrysene, fluorene, or pyrene, as well as to substances in colloidal dispersion. The fluorescent substances are comparatively easily sulfonated by concentrated or fuming sulfuric acid and form water-soluble sulfonic acids.³² The complete deblooming of oils is usually required only for medicinal, or water-white, oils and perfumery oils,* as the fluorescence is often desired in other oils; and it may be imparted artificially, as discussed in later chapters.

Odor

The undesirable odor of petroleum distillates is usually ascribed to various nitrogen and sulfur compounds and to traces of naphthenic acids.³³ The odor is almost always lessened by acid refining. In the case of cleaning solvents, however, avoidance of any residual odor after the solvent evaporates from the clothes cleaned by the solvent is of importance, and the method for treating such solvents is selected with this in mind. For

* Intermediate fraction between kerosene and lubricating oils.

this type of oil, the use of fuming acid should, as a general rule, be avoided, since weaker acids produce less of the residual odor. If possible, the stock should be handled so that no acid treatment is required; a caustic wash should suffice.

The odors emanating from petroleum refineries are variable; they may be due to nitrogen bases released when the acid used in washing petroleum products is later neutralized, or they may come from the alkali extractions of the acidic compounds from the petroleum distillates, especially the cracked products. These alkali extraction compounds are typified by mercaptans, hydrogen sulfide, naphthenic acids, and phenols.

Sulfur Content

The sulfur content of all distillates is usually reduced by refining with sulfuric acid; however, if too little strong acid or a comparatively weak acid is used at a sufficiently high temperature so as to sulfonate the oil, the amount of sulfur in the finished product may be higher than in the original stock. This condition is seldom encountered in commercial practice.

There is no relationship between the total sulfur content of an oil and the type or intensity of treatment to which it must be subjected to give a prescribed sulfur content. Combination of acid treatment with redistillation of the oil with steam or under reduced pressure is usually more effective in removing sulfur than the straight acid treatment, but the cost data determine whether the oil should be redistilled or given a greater amount of acid without redistillation.

Difficulty is usually experienced in desulfurizing certain cracked distillates from California and Mexican petroleum. Though a strong acid, especially 98 per cent or fuming, is fairly efficient, it cannot always be used with success because of high losses of oil and especially of some of the more desirable hydrocarbons. Some advantage has been found in segregating the oil into fractions and treating the individual fractions for sulfur, gum, etc. This procedure is usually not practical because of the increased expense; and, moreover, the sulfur compounds are often fairly evenly distributed through the whole boiling point range of the oil. In cracked distillates the first and the last fractions usually contain less sulfur than the intermediate fractions,^{215, 171} though the reverse may be true with different types of crude oils.⁷¹ During the refining and redistillation, the sulfur compounds are generally more concentrated in the heavier fractions,²¹ but a thorough examination would probably show that the derivatives of the sulfuric acid which remain dissolved in the oil and boil at high temperatures are responsible for this condition. For more data on

sulfur removal, see the section on Temperature of Treatment in this chapter.

Burning Test

Aromatic and highly unsaturated hydrocarbons, asphaltic and bituminous substances, or, in general, hydrocarbons with a high ratio of carbon to hydrogen, as well as sulfur are responsible for poor burning qualities of kerosene. Gurwitsch¹⁰⁸ studied the deleterious effect of the addition of a small amount of asphalt to a kerosene of good burning quality and found that 0.02 per cent of a soft grade of asphalt reduced the illuminating power of the oil by 21 per cent after three hours' burning, and 0.1 per cent diminished it by 60 per cent in four hours. Treatment with sulfuric acid decreases the tendency of the oil to smoke and to form incrustations on the wick fiber, and increases the illuminating power. High-grade kerosenes from asphalt-base crude oils are usually manufactured by treatment with fuming acid rather than with ordinary 93 per cent acid, as the latter is not so effective or economical for removing the aromatic and other undesirable constituents. Treatment with liquid sulfur dioxide (Edeleanu Process) is also employed extensively for the same purpose, and its use is increasing rapidly. The installation of the sulfur dioxide treating process is rather expensive, and it can compete with the sulfuric acid method only when a high-grade kerosene is made, requiring as much as 45 pounds or more of fuming acid per barrel in treating certain types of stocks. This cost comparison is only approximate, as it depends on the cost of the oil, use and value of the by-products, etc. The Edeleanu Process is discussed in more detail in the chapter on Solvents. Kerosene stock from paraffin-base crude oil is usually free from aromatics and requires only mild treatment with acid or adsorbents for conversion into a high-grade kerosene.

The illuminating power of kerosenes generally increases with the increased density of the oil, temperature of the flash and fire points, surface tension, and index of refraction. Fogging of the chimney is greater with more dense oils. Large quantities of easily volatile material should be avoided, as they increase the consumption of kerosene, whereas heavier, less volatile fractions increase the viscosity of the oil, causing excessive smoking and incrustation of the wick. Thorough washing of the oil after acid treatment with caustic soda solution and water is important in order to remove acidic substances and soaps which are formed during the refining. Calcium and magnesium soaps are especially injurious to kerosene. They are slightly soluble in kerosene.

The degree of refining of a sample of kerosene of known characteristics can be determined by tests other than the actual burning test. For exam-

ple, the improvement in the burning quality of a naphthenic-base kerosene can be correlated with the increase in A.P.I. gravity of the oil produced by the treatment (usually about 1.5° to 2.5° A.P.I.); with the decrease in the sludge test; with the so-called ring number of the oil; with the elevation of the distillation-gravity curve, in which the ordinates express the boiling points of the successive fractions distilled, and the abscissas the corresponding A.P.I. gravities; or with the increase in the ratio of hydrogen to carbon in the oil during treatment. Higher temperatures of treatment, within certain limits, are desirable, but subsequent distillation may be required to secure good color.

Unsaturation

As the iodine or bromine value is a rough measure of the amount of unsaturated hydrocarbons in the oil, it decreases during refining. It has been reported to disappear entirely for certain crude oils, but for all American crude oils it does not disappear, though it often approaches a constant value.¹⁰⁸ It is not an absolutely accurate measure of unsaturation, however, because of its tendency toward substitution.

The so-called acid heat test has recently been introduced for measuring unsaturation of aviation gasolines. This test consists in measuring the temperature rise which occurs on mixing gasoline with sulfuric acid (or sometimes with a mixture of sulfuric and nitric acids) under carefully prescribed experimental conditions. Introduction of this test, as well as of the bromine index and similar requirements in gasoline specifications, is rather surprising after publication of a large number of original investigations which definitely show that unsaturation *per se* is not a criterion of gasoline instability because the olefins, which constitute the greatest portion of the unsaturates, are amply stable, whereas the diolefins are unstable and should be removed. Olefins constitute a relatively high percentage of cracked gasoline and are universally accepted as being preferable to paraffins as antiknock agents. It appears that the more reliable stability tests, such as the oxidation test, gum test, etc., are ample, and that the introduction of acid heat or bromine index tests is a step backward in the industry.

Specific Gravity

The removal of asphaltic, aromatic, and unsaturated constituents tends to decrease the specific gravity of an oil.¹⁰³ However, the specific gravity may be increased in the case of certain highly unsaturated oils by treatment with sulfuric acid, especially with small amounts of the acid, because of polymerization to dipolymers soluble in the oil²³⁴ and the formation of dialkyl sulfuric esters, which in part may also remain in the oil. In

contrast, oils refined with solvents such as liquid sulfur dioxide always have lower specific gravities than the original distillates because of the extraction of aromatics and olefins and the absence of polymerization or sulfation products. The actual change in density that may occur is difficult to predict because of the factors mentioned above, and because of the evaporation of some of the light constituents. Thus in treating a certain solar reduced stock, the rise in the A. P. I. gravity was found to be proportional to the treating loss, and for any given loss the change in gravity was practically uniform for all the concentrations of acid between 75 and 98 per cent, the range investigated.²³³ The removal of color was not found to be related definitely to changes in gravity, for color removal is not proportional to the amount of acid used.

It is claimed that by plotting the gravities of the residues obtained from a given crude oil in a series of acid treatments, a curve may be drawn which can be used for the identification of the source of the crude oil, the reaction being called the "Albreaction."¹⁴⁴

Solidification Point

The refined oil usually has a higher freezing, or pour, point than the non-refined oil, and the separation or crystallization of wax may begin at a higher temperature because of the removal of resinous and similar substances which hinder crystallization. The melting point of such substances as vaseline is also higher after the acid treatment, sometimes by 10° F., or more.¹⁰⁸

Antiknock Properties

Acid treatment is usually detrimental to the antiknock qualities of gasolines, though in usual refining this decrease in antiknock value is small inasmuch as the quantity of acid is small; but the loss may be appreciable when the sulfur content is high and large proportions of acid are employed for its removal. However, the lead susceptibility, or the rise in the antiknock rating of gasoline on addition of a certain quantity of tetraethyl lead, is usually increased because of removal of sulfur compounds, which have an unfavorable effect on lead susceptibility. For this reason, if tetraethyl lead is to be added to gasoline, the quantity of lead required to obtain a certain antiknock value may not be increased, and sometimes it is even decreased, by acid treatment, even though the untreated cracked gasoline is taken as the standard to which the antiknock values are referred.^{102, 209}

Oxidation

Highly refined oils, like medicinal oils, *i.e.*, oils refined by fuming acid, may oxidize more readily under certain conditions than the less refined

oils, although they are superior in other respects. The addition of a trace of the original oil or of kerosene distillate is claimed to restore the resistance to oxidation of transformer oils treated with oleum.²³⁹ Reclaimed automobile lubricating oils (mediumly refined oils) are usually reported to be more resistant to oxidation than the original lubricants, provided they are re-refined with acid, clay, etc., and not merely filtered for the removal of suspended matter, an operation which certainly cannot be considered as a reclamation process. It is assumed that the more easily oxidized constituents have been eliminated during use in the motor, and their degradation products removed in the re-refining. However, there is a question whether such oils have been investigated for resistance to oxidation with sufficient care for the application of a general conclusion to all well-refined used lubricants.¹¹⁵

Numerous oxidation tests are applied to lubricating oils, and they are discussed in more detail in subsequent chapters. It should be noted here, however, that some of these oxidation tests may show for the severity of sulfuric acid refining entirely different relationships from the other tests. For instance, the "German tar" test may first show a decrease and then a rise when additional quantities of acid are used. Other tests, such as the Michie test, may show continuous improvement with the quantities of acid used, etc. The oxidation tests by themselves are thus of little value in estimating the quality of an oil unless they are carefully correlated with the service conditions. Moreover, such correlations are not necessarily true for stocks from different crude oils, and a considerable amount of experimental work is always required when refineries change to a different crude oil.

Gum Test

The gummy sediments in gasolines are usually ascribed to neutral alkyl sulfates, to diolefins,³⁸ aldehydes,²¹⁶ and to the oxidation products and polymers of such substances as styrene and indene.³⁴ Organic peroxides are the probable intermediate products.¹⁷⁸

Steam distillation after the acid treatment of gasoline materially reduces the gum content of the gasoline. The gums and the gum-forming constituents are primarily encountered in cracked distillates, and if the gasoline is not to be redistilled, the use of weak acid in the refining will give the lowest content of gums.

There are some advantages in blending certain cracked and straight-run distillates to reduce the gum, the quantity of gum in the blend being reported less than the calculated amount. This phenomenon may be due to the unsatisfactory manner of making the gum test, but there is the possibility of actually introducing natural gum inhibitors from the straight-

run gasoline to the more highly refined cracked gasoline. Preliminary heating of cracked distillates to a temperature above their boiling point and under pressure before the acid treatment has been recommended in order to obtain a product of a minimum gum content and of stable color.²⁹ This subject of gum formation and prevention, as well as the various gum tests, is discussed in more detail in the chapter on Gums in Cracked Petroleum Products.

Viscosity

Viscosity decreases considerably in the ordinary commercial refining of straight-run oils with sulfuric acid, the effect being the more pronounced with the more viscous distillates. Thus the treatment of a certain turbine oil distillate with 48 per cent by weight of 20 per cent fuming acid in twelve consecutive additions decreased the absolute viscosity of the oil at 133° F. from 0.1785 to 0.129, and at 320° F. from 0.01902 to 0.0179.¹ In the case of cracked light distillates, however, an increase in viscosity may be observed, partly from the formation of more viscous polymers and partly from the solubility of the lightest unsaturated constituents in the acid.

It is impossible to make a rough approximation of the change in viscosity of an oil during acid refining, as different stocks vary in their behavior. According to some investigations,²³³ the viscosity of an oil may first increase and then decrease with the addition of larger amounts of acid. Likewise it has been observed that in treating lubricating oils the viscosity may first decrease, then increase, and again decrease with further additions of acid.^{233, 234} Naphthene-base oils, however, have a greater tendency than paraffin-base oils to show this irregularity in the decrease in viscosity with increases in the quantity of acid used. It has been noted in the treatment of a lubricating oil that if the amount of acid is kept constant, but the temperature of the treatment is varied, the viscosity of the finished oil may not be changed up to a treating temperature of 170° F., but it then is increased rapidly with further rises in the treating temperature.²³⁵

Lubricating Oil Qualities

Vital tests for quality in an automobile lubricating oil are very meager. The oil should resist decomposition under the heating to which it is exposed and should possess high resistivity to oxidation, which produces organic acids and "sludges." All petroleum lubricating oils seem to possess ample adherence to the bearing metals, or wetting power, except on a few very special surfaces, as on the heavy-duty worm gears, and this property is not materially affected by the amount of acid used in refining. These

characteristics of oils are discussed in later chapters along with methods for improving them when necessary.

The relatively high viscosity of a lubricating oil at all temperatures is one of its very valuable characteristics, and the less the viscosity drops with rise in temperature, the more valuable the oil is. This last property is usually referred to as the "viscosity index" of the oil. It is usually found that acid treatment raises the viscosity index, although to a less extent than when the oil is refined by solvents.

Ash Content

Petroleum distillates usually contain negligible quantities of ash constituents; but during acid treatment and the subsequent alkali wash, the quantity of mineral salts usually increases because of the formation of soaps of naphthenic and sulfonic acids and of sodium sulfate, which to a slight extent are retained in the oil.¹⁰⁸ It is possible, however, to decompose the soaps with acid and to hydrate the sodium sulfate with water and methyl alcohol at 150 to 200° F. The resulting $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is then removed from the oil by settling.⁸⁶ Other methods of reducing the ash content of lubricants are discussed in the chapters on Treatment with Alkaline Reagents and Refining by Adsorption.

Losses from Acid Treatment

Refining losses are due to the formation of polymers and alcohols and to extraction of some of the hydrocarbons with sulfuric acid. Polymerization losses in light oils can be estimated by the four point distillation control method.¹³⁷ In treating some of the cracked distillates at normal temperatures with large amounts of acid for sulfur reduction, the polymerization losses may reach 15 to 20 per cent of the original raw material.^{110, 171} This heavy loss occurs only in the treatment to reduce the sulfur content to around 0.10 per cent when the initial sulfur content of the gasoline is especially high. For California cracked naphthas the losses are usually less than 5 per cent when refining with about 10 pounds of concentrated acid per barrel of oil; and for the Mid-Continent crude oils, which are refined with not over 5 to 6 pounds of acid per barrel, the losses do not exceed about one per cent.¹⁶⁷ Polymerization losses are always very much less in the low-temperature treatment,¹¹⁰ and they decrease with decreasing strengths of acid.

A little of the acid applied in refining becomes spent through oxidizing the oils and is reduced to sulfur dioxide; and some combines with the oil constituents, especially in cracked distillates and at higher temperatures. A great increase in the loss of acid is always observed when the strength of the acid, calculated as H_2SO_4 , exceeds 100 per cent. Sulfur trioxide

has a powerful oxidizing action on oil. The reduction of sulfuric acid to sulfur dioxide is much less in the low-temperature treatment.

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Chapter III

Sulfuric Acid Sludge and Hydrogen Sulfide; Recovery and Manufacture of Sulfuric Acid

As pointed out in the preceding chapter, strong sulfuric acid acts on many constituents of petroleum oils, forming solution and reaction products which for the most part stay associated with the acid as a viscous liquid or semi-solid material, known as acid sludge. This sludge is insoluble in the oils, and because of its greater density settles out more or less completely. Asphaltic-base petroleum oils bear a much higher percentage of chemically reactive compounds than paraffin-base oils, and consequently more sulfuric acid is required to refine them to stable products, and more acid sludge is produced during refining. In some of the largest refineries much more than 100 tons of acid sludge is formed daily. The acid content of the sludge depends on the oil from which it comes and on the method of refining; the acid may vary from 20 to 75 per cent of the sludge.

The acid sludge from residual and heavy lubricating oil stocks usually contains a small ratio of acid to organic matter, is very viscous, and may become solid on standing a short time. The acid of such a sludge is difficult to recover unless the sludge is first mixed with a large amount of the thin and highly acid sludge from lighter distillates. The acid sludge from the lighter distillates, such as gasoline, kerosene, and transformer oils, is fluid; the proportion of acid to organic matter is large; and the acid is fairly easily recovered.

The disposal of acid sludge has long been a problem to every refiner. During the last few years, more economical methods of handling this by-product have been developed. The methods of utilizing acid sludge are varied; it may be burned immediately as fuel; the acid may be converted by means of ammonia into ammonium sulfate; or it may be regenerated (a) by hydrolysis with water, separation, and reconcentration, or (b) by heating the sludge without water to reduce the acid to sulfur dioxide and reconverting the sulfur dioxide by means of catalysts into fresh acid of any concentration, including fuming acid.

When recovered by hydrolysis with water and reconcentration, the acid is dark in color (black acid), but it is just as good as fresh acid for treating most oils. The carbonaceous material left after the hydrolysis and separation of the acid has for the most part been used only as fuel,

although it is much more reactive chemically than the main constituents of the petroleum and should be suitable for the manufacture of valuable chemical products.

The organic material in the acid sludge is complex in nature. It is the result of reactions of the sulfuric acid on different constituents of the oil, such as the reactions with alcohols and unsaturated hydrocarbons to yield mono- and di-alkyl-sulfuric esters; formation of alcohols from olefins; sulfonation of aromatic compounds; direct combination with nitrogen bases; oxidation (strong acid not only oxidizes constituents of the oil when first contacted, but may continue for many days to oxidize the organic constituents of the sludge with evolution of sulfur dioxide); coagulation of resins and asphaltic material; polymerization of unsaturated compounds; condensations; etc. Naphthenic acids are miscible in all proportions with strong sulfuric acid; and such a solution, along with all acid sludges, doubtless dissolves some of the oil or distillate being treated. Certain other substances are soluble in sulfuric acid or form more or less unstable compounds with it. The proportion of organic material to the sulfuric acid in the sludge depends not only on the nature of the stock but on the strength of acid and the temperature of treatment, increasing with stronger acid and usually with higher temperature. The percentage is also higher for treatments with a small amount of acid than with a large amount, other conditions being equal. This result is obvious, since the most reactive constituents respond to a small amount of acid and are removed; the less reactive constituents are affected only by a larger amount of acid. Likewise, in the application of the acid in fractions, or in different dumps, the first fractions of acid yield the highest percentage of organic material in the sludge, and the succeeding fractions yield decreasing percentages.

Because of these variable conditions and the refining of products to meet various specifications, acid sludges possess no uniform physical characteristics. When California cracked gasoline distillates from gas oil of about 26° Bé. gravity (light) are treated at 70 to 90° F. with 10 pounds of 93 per cent acid per barrel (42 gal.), they produce a sludge containing from 40 to 60 per cent free sulfuric acid (titrated in the cold with the use of methyl orange indicator), and have a gravity of 38 to 45° Bé. (heavy). Kerosene stock from asphaltic petroleum must be treated with at least 20 to 45 pounds of 98 per cent or fuming acid to yield a product which will not smoke a lamp chimney as normally tested. The sludge from such a treatment contains about 50 per cent free sulfuric acid, as indicated by titration with an alkali solution.

Gurwitsch ⁴⁰ describes acid sludge from a Galician kerosene distillate as containing 10 to 30 per cent of organic tar, 52.1 to 62.8 per cent free sulfuric acid (precipitated by barium), and up to 8 per cent of sulfuric acid

in the form of sulfonic acids, or sulfuric acid esters. Unfortunately he does not state the proportion or concentration of the acid used in the treatment.

An analysis of a certain sample of fresh acid sludge, obtained in the refining of heavy oils, showed 1.37 per cent of sulfur dioxide, 47.6 per cent of sulfuric acid, 13.5 per cent of mineral oil, 25 per cent ether-soluble constituents, and 0.05 per cent of arsenic trioxide. The amount of sulfur dioxide would increase as the sludge aged.

Table 24 indicates roughly the variations noticeable in sludges.¹

Table 24. Representative Acid Sludges.

Type of Sludge	Sp. Gr.	% H ₂ SO ₄	B.t.u./lb.
Naphtha	1.41	28.50	16,425
Kerosene	1.43	48.50	6,940
Refined oil (high sulfur kerosene)	1.66	76.60	Not burnable as such
Pressure distillate	1.41	52.20	7,700
Gas oil	1.22	30.97	11,155
Heavy lubricating oil	1.37	67.07	9,000
Medium lubricating oil	1.19	24.70	11,850
Wax (m. p., 50° C.)	1.77	78.00	Not burnable as such

The amount of sludge formed in the refining of oils is variable. Non-viscous distillates may lose from 0.5 to 8 per cent by volume to sludge during the acid treatment; cylinder stocks may lose as much as 30 to 40 per cent.⁵⁰ In refining certain oils, such as tree spray oils or medicinal oils, the losses to sludge may reach 60 per cent.

VARIOUS METHODS FOR DISPOSAL OF ACID SLUDGE

As mentioned in the discussion of refining with sulfuric acid, in limited cases the fresh acid sludge can be used for pretreating, or even for treating, some petroleum products. Thus the heavy still bottoms left from distillation processes are sometimes treated directly with the acid sludge with fairly satisfactory results.³⁶ However, only mobile or fluid sludges are suitable for this purpose, for the heavy sludge obtained in refining heavy oils, such as heavy lubricating oil distillates, is a solid or semi-solid product when cold, and cannot be so used. The disposal of the latter is more difficult. The use of acid sludge from especially light oils for treating heavy oils may be objectionable because of its tendency to affect the viscosity and the flash point of the heavy oil.⁶⁶ Sludge acid has been used, according to one patent,⁸⁷ as a treating agent for removing sediment-forming substances from cracked residuum to make it a more satisfactory fuel. An inert material, like coke, may be added to the mixture to facilitate filtering the sediment from the oil. Heavy acid sludge has been proposed for use in the manufacture of artificial asphalt.

Bolgar⁸ prepares artificial asphalt by heating tarry matter with acid sludge at 250 to 400° F. and settling the resulting mixture. Forward and Davidson,³¹ as well as others, propose a variety of methods for preparing asphalt from acid sludge. So far as the authors know, however, no high-grade asphalt has as yet been made from acid sludge, probably because of the difference in properties of asphaltenes in oil and in acid sludge. The asphaltenes in the sludge are believed to be not the true asphaltenes but their derivatives of sulfuric acid of the oxonium type.

Formerly, the type of acid sludge, whether from heavy or light oils, largely determined the selection of the method of disposal. In the newer development of regenerating the acid by heat decomposition of the undiluted sludge, the type of sludge is no longer so important. Since different methods have been devised for handling the sludge, the selection of the most economical one can be made only after proper investigation.

In small refineries, acid sludge is sometimes diluted with water, partly or completely neutralized, and discharged into sewers, a practice more common in earlier times. Sometimes a preliminary separation of oil from sludge is made, and the acid then discharged into sewers. In one process⁶³ the acid is separated from lubricating oil sludge by diluting it with water, settling, neutralizing the remaining acid with lime (17 to 20 per cent of lime is required), and extracting the oil-soluble substances, which are later used for fuel, by means of gasoline. The acid sludge can also be discharged into a sump or pond, and the separating hydrocarbons skimmed off and burned. These methods are applicable only to a limited extent and in isolated places, as large quantities of acid discharged into rivers or seas affect the animal life; and acid discharged into sludge ponds gradually contaminates the ground, a condition which may injure the vegetation of the surrounding territory and bring consequent liability or damage suits.

A simple method of disposing of acid sludge is to burn it.²⁶ This method usually, if not always, involves financial loss because of the corrosive action of the acid on boiler equipment, the labor required, and failure to recover any products.⁴⁶ Moreover, when the sludge is burned, each pound of acid in the sludge releases about two-thirds of a pound of sulfur dioxide, and the sulfur dioxide from the chimneys may be poisonous to surrounding plant life, so such operations may not be permitted in agricultural districts.

To avoid corrosion of equipment in the burning of acid sludge, it is necessary that no condensation of moisture be permitted. In the absence of moisture, neither sulfur dioxide nor trioxide seriously affects the equipment.

A few refineries mix the heavy sludge with fuel oil and alkalis and agitate the blend with steam to produce a homogeneous mixture, which is burned.⁸¹ For this purpose, fresh sludge is pumped to an agitating tank, where it is mixed with about 50 per cent by volume of fuel oil and a small

amount of lime or soda ash, which serves as an emulsifying agent, and is kept agitated at about 120° F. The quantity of fuel oil added to the heavy sludges must be as great as 50 per cent, or the product is too viscous to handle.^{13, 80} The acid sludge and heavy fuel oil must be blended very thoroughly to avoid the possibility of clogging burner tips and valves. Mekler⁶⁰ says that about three to four hours are required to add acid sludge in small portions to the fuel oil, which is kept agitated with air, and ten more hours for circulating the mixture in a storage tank to prepare a satisfactory mixture. From the agitating tank the mixture is circulated through feed lines to the burners, a part being by-passed back to the agitating tanks. It is difficult, however, to keep the sludge suspended in the oil by the agitation, to keep the lines to the burners open, and to maintain the temperature at 120° F. The operation of this process involves a large expenditure of power and depreciation of equipment.

Other proposed processes involve mixing acid sludge with fuel oil, gas oil, and similar material, without the addition of alkalies, and homogenizing, or agitating, the mixture as it flows through a confined passageway.⁵ Special burners and boilers are devised for burning such mixtures.⁵¹ Two types of burners are in general use: the rotary type, and the air-oil injection type. The rotary type, however, seems to be the more satisfactory in actual service. Hinde⁴⁶ has patented a process of disposing of the sludge by using a special horizontal furnace for burning it progressively, first expelling the water and then decomposing the sulfuric acid into sulfur dioxide. The resulting sulfur dioxide is diluted with air and discharged into the atmosphere.

Certain companies have had some success in disposing of the very heavy sludge, or sludge which has become hard and coke-like on long standing, by burning it like coal directly in furnaces. For this method it is necessary to build a bed of hot coals on the grates to a thickness of two to three inches. The sludge is cut into six-inch cubes and placed on the layer of hot coals. After the pieces of sludge are reduced to coke, they are broken up, and the successive layers are added until the fuel bed is built to 12 or 13 inches, a thickness which is maintained. Heat is regulated by admitting air through an opening at the back of the grate. The thick bed is required to prevent the sludge from melting and dripping through the grates. The flue gases are not corrosive while hot, for then there is no water present in the liquid state to form water solutions of the sulfuric or sulfurous acid.^{69, 80}

In another process, acid sludge is agitated with alkalies to form an emulsion; any water which settles out is withdrawn, and the residue is burned with or without the admixture of fuel oil.⁵⁷ Practically all acid sludge, excluding that from the heaviest lubricants, can be neutralized and

mixed with fuel oil without serious difficulty, except that involved in the special handling of the water content. It is often possible to remove much of the acid from the sludge by dilution with a little water (one-third by volume, or less) and heating the whole with live steam. The oil layer can be neutralized later by the addition of alkalis. Sodium carbonate is cheap, but it must be added with care to prevent foaming because of the carbon dioxide evolved.⁵⁰

Heavy sludge can be burned either after separation of the acid or while containing even as much as 20 to 50 per cent of acid. In the first procedure, the acid is separated, and the remaining oily layer is usually, but not necessarily, blended with another oil (gas oil, fuel oil, etc.) for reduction of viscosity, and burned. In the second procedure, the oils are blended without removing the acid, but constant agitation may be required to prevent separation of the oil and sludge. Brass pipes, bronze or Monel-lined pumps, and bronze fittings inside the boiler house are generally used.¹¹

Wilson⁹³ has recently described the different methods of handling various types of acid sludge so that the sludge can be diluted with water and separated into weak acid and acidic tar and the latter burned, or the sludge burned as a whole.

Other less important methods proposed for sludge disposal without recovering the acid are given, since they may suggest some items of interest, though in themselves they may not be immediately practical. They are: mixing of acid and alkaline sludges, treating the mixture with steam, and recovering sodium sulfate and the separated oil;³⁰ decomposing the sludge into sulfur dioxide by spraying it with air into a hot chamber;⁶ and distilling the sludge in closed vessels at progressively increasing temperatures in order to obtain a light oil, a more or less pure coke, and sulfur dioxide.¹⁶

One patent specifies that the sludges be completely neutralized by the gradual addition of solid sodium carbonate, lime, calcium carbonate, or barium carbonate, with or without coal, sawdust, residues, or inert material, and the mixture be heated to high temperatures to produce sulfides.⁸⁹

In another patent, the acid sludge is treated with water and calcium hydroxide, and the oil distilled to yield hydrocarbons and a residue of coke and mineral salts.⁹⁷

An extremely old patent states that the acid separated from acid sludge, with or without an addition of potassium sulfate, can be neutralized with ammonia vapors to give a product suitable for use as a fertilizer.²⁹

By-products are obtainable from the acid sludge. Thus bitumen can be made from the acid-sludge tar produced in treating crude oil with sulfuric acid.⁷³ In one patent, the acid sludge is treated with potassium bichromate to produce fatty acids by oxidation. The volatile fatty acids

are distilled with steam, and the non-volatile fatty acids are skimmed from the aqueous chromate solution and converted into soaps. Certain patents claim that the saponifiable material remaining in the oil after separation from the sulfuric acid can be isolated by first neutralizing the oil with alkalis and then separating the soaps.⁵⁶ Sludges contain various alcohols (particularly the sludge from cracked gasoline), which can be distilled from the diluted acid and used as denaturants. The heavier fractions are claimed to be convertible into insecticides, varnish substitutes, and lacquers.⁷⁰

Karskii and Kapatzinskii⁴⁹ claim that up to 60 per cent of an asphalt suitable for varnish is obtained by blowing air through a mixture of 2 parts acid sludge, 1 part turpentine, and 1 part wood tar at 536 to 570° F. for 18 to 20 hours. It is of interest to mention here that when a solution of asphaltenes in carbon bisulfide, carbon tetrachloride, or similar solvents, dries out, the resulting film peels off very easily; but when turpentine is used as a solvent, a durable film is formed.

For many years certain types of sulfonic acids have been manufactured as by-products from the treatment of oils, especially kerosene and the white medicinal oils, with fuming sulfuric acid or sulfur trioxide. The purified sulfonic acids are best known as the mahogany acids or sulfonates. In the manufacture of these sulfonic acids, the oil is treated with successive additions of acid, and the sludge removed after each addition; but only the sludge from the latter additions is used for the commercial sulfonates. These sludges, produced after the oil has already been heavily acid-treated, differ from the sludges from the first additions of acid and differ among themselves, some being more soluble in oil than in water (the "mahogany acids"), and others being more soluble in water than in oil (the "green acids").²⁷ These acids are used as emulsifiers,²⁵ as well as de-emulsifiers, and in many other ways.

Petrov⁶⁸ makes sulfonic acids from acid sludge by first diluting the sludge with water in equal parts, heating the mixture in an autoclave for three to four hours at 20 atmospheres, distilling the oily layer, and later sulfonating the fractions of oil thus obtained. Such sulfonated oils can be used in saponifying fats in place of the Twitchell reagent in the soap industry. This operation seems to have potential value.⁴⁰

The acids⁹⁰ can also be obtained from kerosene acid sludge by passing sulfur trioxide diluted with air through the sludge or, preferably, through the oil or tar separated from the acid sludge. The acid sludge from some oils can first be subjected to extraction with a mediumly heavy hydrocarbon oil; then the residue is diluted with water, allowed to settle, and the dilute sulfuric acid layer drawn off. The sulfonic acids are then separated from the acid, in which they are dissolved, and purified. They are moderately soluble in ether and freely soluble in amyl alcohol.⁴⁷ Wolff⁹⁵

uses alcoholic alkali solution to neutralize acid-treated oils and to extract the sulfonic acids. He then recovers the sulfonic acids from the alcohol solution.

Ellis²⁷ gives a comprehensive discussion of the sulfonic acids and their many uses. The patent literature should be consulted for additional details of the manufacture of these acids; some of the typical patents are enumerated in the bibliography at the end of this chapter.^{21, 31}

The Shell Development Company has many patents⁷³ on the important industry of treating the sulfuric acid sludge with ammonia and producing thereby ammonium sulfate and a hydrocarbon liquid suitable for fuel. The ammonium sulfate is used primarily as a commercial fertilizer.

Acid sludge can be used for the production of hydrochloric acid by heating it with sodium chloride and water. The resulting sodium sulfate solution can be withdrawn from beneath the tarry substances, and the latter used as a road binder.⁵³

It is thus recognized that the organic constituents of the sludge are chemically active, and doubtless they will be developed more extensively.

SULFURIC ACID FROM ACID SLUDGE

In the last few years the production of sulfuric acid from acid sludge has become an important operation in all the large refineries throughout the world. In the United States, over a million tons of acid are produced annually from the acid sludge. In practically all of the refineries, the saving in the cost of acid is appreciable, and the former annoyances in disposing of the acid sludge are greatly diminished.

Two general processes have been developed for obtaining sulfuric acid from acid sludge:

- (1) Heating the acid sludge with water to cause it to separate into layers: a hydrocarbon liquid still containing a small amount of acid, an aqueous layer of sulfuric acid. The oil is burned as fuel, and the weak acid is reconcentrated to a fairly strong acid.

- (2) Heating the acid sludge to about 500° F. in a continuously operating kiln. The sulfuric acid is reduced to sulfur dioxide, and the latter reconverted into fresh sulfuric acid.

The two methods will be discussed in detail, the method of hydrolysis and reconcentration being considered first.

As indicated above, the recovery or restoration of sulfuric acid from acid sludge by hydrolysis for re-use on oil products, or otherwise, consists of two distinct stages: separation of the acid from the oil or carbonaceous material, with which it is associated, by diluting with water and heating and concentration of the resulting weak acid. Only sludges from light oils can be utilized economically in this manner. No generally satisfactory

method of separating the acid from the lubricating oil sludges has yet been devised because of their high viscosity and because of the complex carbonaceous material which they contain.

It may be noted that in very special cases, acid sludges from heavy oil can be handled in this way. Staley⁴⁶ has described a commercial plant for treating lubricating and cylinder stock sludges, which he reports as successful. Clean acid, with a content of 15 to 40 per cent sulfuric acid, and fuel oil are obtained.

Separation of Acid Sludge into Acid and Oil

The sludges derived from paraffin-base oils are usually fairly easily separated into their organic constituents and sulfuric acid, but the sludges derived from naphthenic- or asphaltic-base oils are separated with greater difficulty. The latter sludges often are separated more satisfactorily when heated under pressure.⁹⁸

For separation at atmospheric pressure, the acid sludge is first diluted with water (25 to 50 per cent of the volume of the sludge) and agitated by air, steam, or other means. In some sludges, especially from light paraffin-base oils, the separation of oil and acid may be sufficiently complete from the heat of dilution without the aid of further heating. Experiments determine what dilution is necessary and best. Usually enough water and steam are added during the process to yield a separated acid of from 35 to 55 per cent sulfuric acid content. The concentration is kept as high as possible since the water must later be evaporated.

In older patented processes, De Bataafsche Petroleum Maatschappij¹ adds sufficient water to yield acid of 52° Bé., and Rütgerswerke A.-G.⁷¹ dilutes the acid sludge with one-third its volume of water. Millochau¹¹ adds 40 per cent by volume of water to the acid sludge, separates the two layers, and washes the oil with a 20 per cent caustic soda solution.

In one modification, which is patented, the sludge is diluted with water; then the oil is distilled rapidly in order to prevent as far as possible the decomposition of the acid.⁷ This procedure permits separating only part of the oil. In an old patent, the sludge is diluted, settled, the oil evaporated, the acid again diluted with water, and the procedure repeated until the oil is completely separated from the acid.⁵⁴ In another modification, two successive washings of the oil separated from the acid sludge are recommended, the weak acid from the second washing being used in the first washing of a succeeding fresh batch of sludge.³⁰ An early patent suggests treating the acid sludge with cold water to remove most of the free acid, then treating the separated oil, which still contains some acid, with an alkaline solution and heating to dissolve sulfonic acids (and to neutralize the sulfuric acid content).³²

In another old patent, the sludge is treated with water and steam for separation,⁶⁷ and in a later patent steam alone is claimed to be efficient;²⁰

but in this method the oil would doubtless be coked, and much of the sulfuric acid reduced to sulfur dioxide. It would not be practical for most acid sludges. It was early seen that the offensive vapors produced in such treating processes should be conducted to a furnace and burned unless the refinery were located in an isolated district.¹⁵ The use of closed retorts (pressure separation) for heating and separating the diluted acid sludge permits easier control of the odors than open tank separation in that the odoriferous gases can be sent as desired to fume furnaces and burned. The concentrators can likewise be controlled so as to be made odorless.

Digestion of the sludge in open tanks with water and steam, or with dilute acid recovered from sludge, and then heating with steam until the oil constituents are converted into pitch is described in a patent issued to Gray.³⁷ It is pointed out that air agitation aids this digestion and yields a much thicker oil.³⁸

Good separation, desirable in all cases, is obtained by heating the diluted acid in an autoclave at 285 to 340° F. and at a pressure of about seven atmospheres.^{4, 91} The steam and the vapor of the light oils in the sludge in the retort are usually ample to give an excess pressure and to prevent undue agitation and emulsification of the oil and acid from the turbulent boiling. Various other patents have been issued on methods of separation. In one very similar to the foregoing, the acid sludge is mixed with an equal volume of water and heated for about eight hours at 302 to 356° F. in an autoclave.⁹² In other patented processes steam introduced into an autoclave at high pressure is used to advantage to hydrolyze diluted acid sludge. The sludge is diluted with water and maintained at 325° F., or above, the heat being applied internally with live steam.⁴⁵ A continuous process of a similar nature has been devised and, with certain modifications and in combination with the two preceding patents, has found extensive application.^{19, 41, 42} According to another report, the sludge is maintained in the autoclaves at a pressure slightly above that at which the acid boils in order to effect good separation of the dilute acid and oil. In this condition, the oil has very low viscosity and permits the acid content to settle quickly.¹⁹ The hydrolyzing chamber is constructed so as to retain the separated acid for a longer time than the oil, the oil being removed from the top of the chamber nearly as fast as it separates.⁴²

If sludges from light and heavy oils are available, it is, in general, recommended that they be mixed so as to facilitate the separation of the acid from the heavy sludges, since the latter are by far the most difficult to handle. Sludge can also be mixed with gas oil or "cycle stock," or with steam still bottoms from the distillation of acid-treated cracked gasoline, and the hydrolysis effected by means of water and steam. The thinning effect of these added oils permits the acid to settle more completely

from the oil.²³ Kerosene stock instead of the gas oil is usually best suited to facilitate the separation of other sludges. Likewise the acid sludge can be agitated with light oils, tar oils, anthracene oils, creosote, phenol, etc., after preliminary dilution with water, to make the separation of the sludge oil more complete.¹⁴

In the separation of the tarry material from the weak acid when heated to 325 to 350° F. in retorts, especially in continuous operations, it is desirable to remove the oil almost as fast as it rises from the acid to prevent decomposing it to coke through the necessarily prolonged heating.

Of the processes just described for separating the oil and acid, only those which include diluting with water and settling or diluting with water and heating at the various temperatures and pressures have thus far become of commercial importance; other processes are either too expensive or do not effect sufficiently complete separation. Thus the diffusion of sulfuric acid from sludge through porous membranes yields colorless acid, but the acid is still contaminated with organic and sulfo-acids. The organic matter decomposes in the concentrating of the acid, and the acid again turns black.⁹⁴

The addition of various chemicals to the weak acid which separates on diluting the acid sludge with water and which still contains appreciable quantities of organic matter, is specified in many patents; but these processes are as yet of little interest, and only a few will be mentioned. The addition of methyl alcohol in closed apparatus, while the whole is heated and stirred, has been patented.⁹² One patent proposes treating the separated weak acid with decolorizing earth, silica gel, or animal charcoal; or with substances which may coagulate or resinify, such as phenol, sodium phenolate, formaldehyde, and alkali silicates; or with water and gasoline, benzene, Tetralin, or like substances; or with substances of strongly aliphatic or polymethylene character.²¹ A small proportion of phenols gives fairly good results in clearing the color of an acid of 36 per cent strength, but a similar treatment of a more concentrated acid is ineffective. Electrolytic oxidation of the carbonaceous material in the separated acid³³ produces a colorless acid, but it still contains a high percentage of carbonaceous material, and the treatment is thus of questionable value.

The oily substances which are separated from the acid sludge and now used principally for fuel should be thoroughly investigated for other possible applications. Much of the oil can be distilled from the dilute acid with the aid of steam, as discussed elsewhere in this chapter. A high percentage of this oil has about the same boiling range as the distillate originally treated with the acid. It is relatively rich in sulfur compounds and is odoriferous. Resins are obtainable from the sludge oil by treating

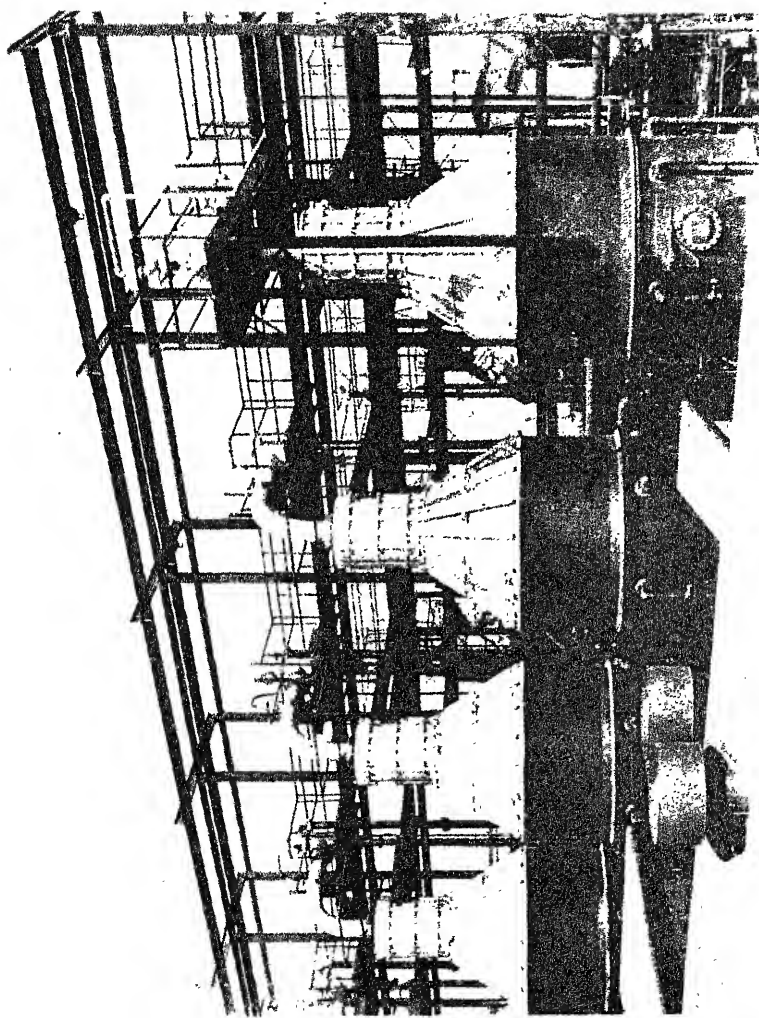
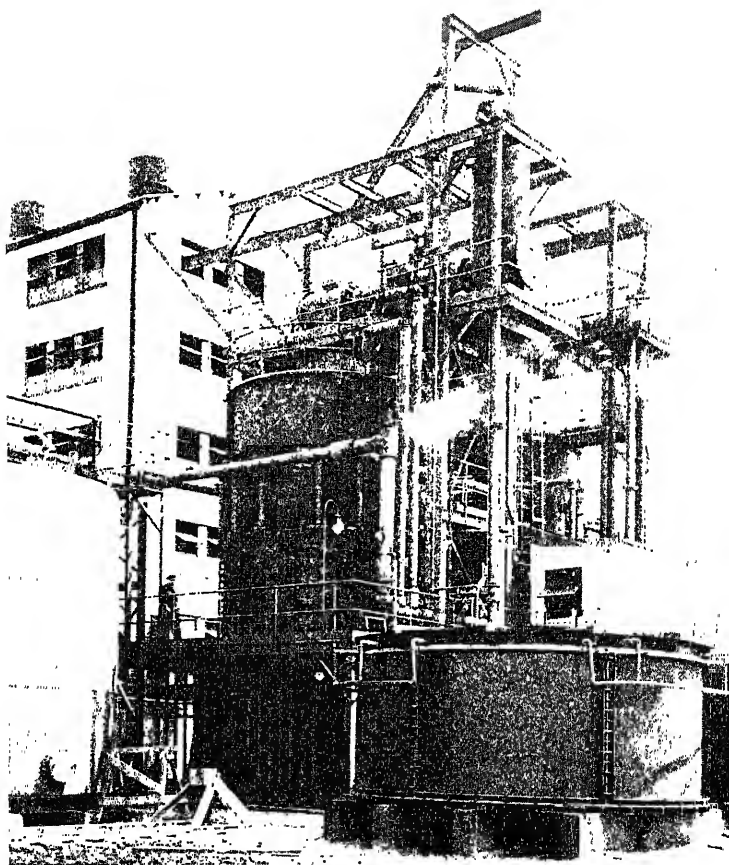


FIGURE 6. A Plant of Four Simonson-Mantius Vacuum Sulfuric Acid Concentrators.
Capacity, 80 Tons of 65° or 280 Tons of 60° Acid per day.
Courtesy, National Lead Co.

it with sulfur at elevated temperatures, a procedure which also is supposed to reduce the remaining sulfuric acid to hydrogen sulfide.⁷⁶

Concentration of Acid Separated from Acid Sludge

Many processes have been proposed for concentrating the dilute acid obtained from acid sludge by separating the oily material from the acid



Courtesy, National Lead Co.

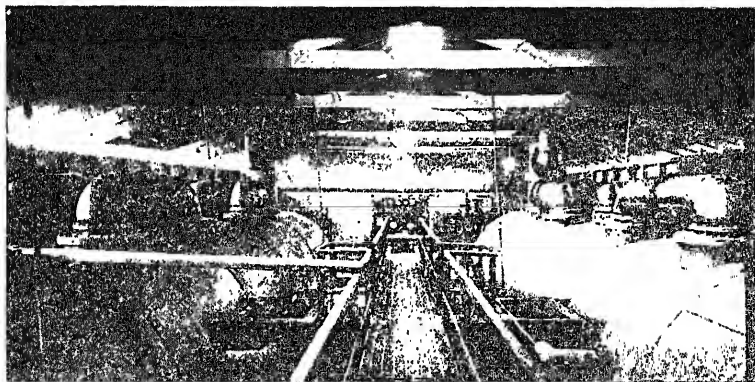
FIGURE 7. One type of Mantius Vacuum Sulfuric Acid Concentrator.

of the acid sludge. The old methods of concentrating the acid in lead or glass pans are no longer in use; they are not practical because of the decomposition of the acid by oxidation of the organic matter at the elevated temperatures necessary, and because of the high cost of operation. The old-type tower concentration is also impractical for the same reasons.

The Skinner tower concentrator, which is an improvement over pan and still sets, is described in the literature.⁷⁹ It is useful for small quantities of acid if they do not contain any appreciable amount of organic matter.

Various companies install in refineries complete acid recovery equipment guaranteed to restore acid of satisfactory quality within certain cost limits. The two most widely used processes are that of the National Lead Company, known as the Simonson-Mantius Vacuum Process, and that of the Chemical Construction Corporation, known as the Chemico Process. Photographs of both types of plants are shown in Figures 6, 7, and 8.

In the modern methods of concentration, the temperature of evaporating the water from the acid is lowered either by evaporating under vacuum or by forcing a blast of hot air through the acid.



Courtesy, Chemical Construction Corp.

FIGURE 8. Two "Chemico" Drum Type Two-stage Acid Concentrators. Total Capacity 50 tons of 66 Bé. Acid from 30 Bé. Acid.

In the Mantius Vacuum process the acid is heated indirectly by means of coils or tubes through which high-pressure steam is passed. Either batch or continuous concentration is employed, depending on the quantity or type of acid. This method has satisfactorily met the requirements for concentrating with a good yield all the various types of weak sludge acid to a strong acid having a high ratio of H_2SO_4 to free water. Former difficulties caused by the foaming of certain types of sludge acid have been overcome by the use of very high vacuum in the Super Vacuum Concentrator. Owing to the low boiling temperature of the acid, losses by distillation are exceedingly small, and no fumes are given off by the concentrator.⁷⁸

Concentration by a current of hot air blown through the acid has been found practical for all sludge acids. Doubtless the air has some tendency

to oxidize the hydrocarbons still remaining in the separated sludge acid and thus lessens their power to reduce the sulfuric acid to sulfur dioxide. It also lessens the tendency to foam. It is often indispensable in both processes to concentrate in two stages in order to avoid foaming and undue loss of acid.⁶⁴

Modifications of the two-stage concentration by hot gases have been made the subject of a patent by Mast.⁵⁹ The improvements, which simplify the process, have been combined with the former process of the Chemical Construction Corporation, and the new apparatus is known as the Chemico Drum Type Concentrator. In this later process, the hot air, or gas, is blown countercurrent to the acid, being passed first through the stronger acid and then through the weaker acid. The weak acid is continuously passed into the second stage of concentration before it becomes heated and concentrated to its foaming temperature, the second stage being kept above its foaming temperature. The rates of flow of acid and air are adjusted to yield acid of the desired concentration. The hot gases are produced by burning gas or oil and diluting with air to give a temperature of 1100 to 1200° F. After the hot gas is passed through the more concentrated acid, its temperature is about 400° F. It then enters the weaker acid, emerging at about 200° F. Provision is made, however, for by-passing some of the hot gas directly to the weak acid for ease of control of temperature in the two stages. From the concentrator units, the gas is passed directly into the atmosphere or preferably into a Cottrell electrical precipitator, where any entrained acid, or acid mist, is collected and returned to the concentrator.

It is necessary that the apparatus for concentrating the acid be constructed of or lined with material which resists the hot acid and withstands the strains of changes in temperature. In the Simonson-Mantius Vacuum Process and the Chemico Process, the concentrating units are lined first with lead and then with one to three layers of acid-proof brick, laid in acid-proof cement.

Some of the large petroleum refineries manufacture fresh sulfur trioxide and fuming sulfuric acid by the contact process for use in fortifying the recovered acid. In the recovery of the spent acid the over-all yield, based on the amount of acid used in treating the petroleum distillates, averages about 66½ per cent; hence the amount of fresh acid required to replace the loss averages about one-third of the total acid used. Several factors make the manufacture of acid in the refineries economical. The anhydride and extra-strong fuming acid cannot be conveniently manufactured at a distance and shipped to the refinery for blending; but if manufactured in the refinery, the acid can be absorbed as fast as produced in bringing the weaker recovered acid to a high concentration. The new sul-

furic anhydride combines with the water of the weak recovered acid and obviates concentrating the recovered acid to as high a percentage as otherwise would be necessary.

Table 25. Degree of Concentration of Recovered Acid Required when Fortifying with Fresh Acid of Different Concentrations.

Case I.				
Refinery requirements—30 tons per day, 93% H_2SO_4 .				
Restored acid available—20 tons per day, "93% equivalent."				
Fortify with	A 93%	B 98%	C 104½%	D SO_3
Source	Purchased	Purchased	Purchased	Con. Plant
Actual tons fortifying acid required	10.00	9.38	8.99	7.99
Actual tons restored acid required	20.00	20.62	21.01	22.01
Strength of restored acid required	93.0%	90.7%	88.2%	83.0%

Case II.				
Refinery requirements—30 tons per day, 98% H_2SO_4 .				
Restored acid available—20 tons per day, "98% equivalent."				
Fortify with	A 98%	B 104½%	C 109%	D SO_3
Source	Purchased	Purchased	Purchased	Con. Plant
Actual tons fortifying acid required	10.0	9.38	8.99	7.99
Actual tons restored acid required	20.0	20.62	21.01	22.01
Strength of restored acid required	98.0%	95.1%	93.3%	89.1%

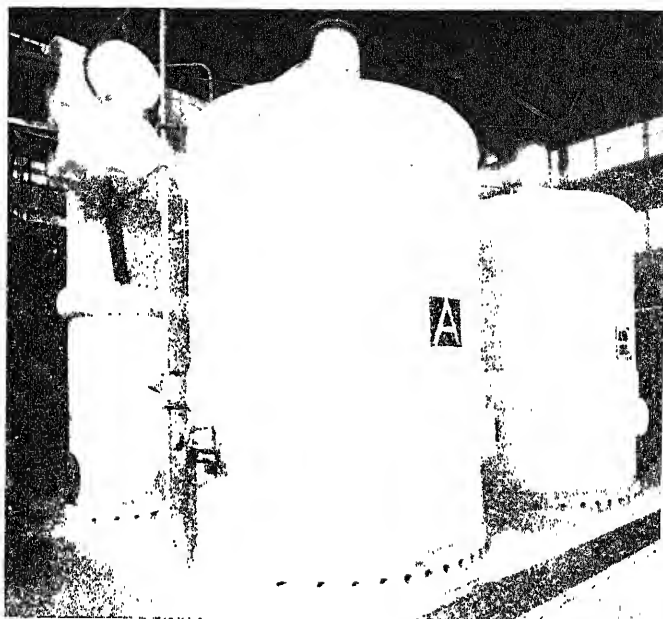
The data of Tables 25 and 26 on the advantages of manufacturing fresh strong acid in the refinery were calculated by Gilchrist,³⁵ former president of the Chemical Construction Corporation, on the basis of an over-all 66⅔ per cent recovery of acid, or on a cycle efficiency of 66⅔ per cent.

Table 26. Water Evaporated in Acid Concentration.

Case I.				
Tons water evaporated to make 20 tons acid "93% equivalent."				
	A 93%	B 90.7%	C 88.2%	D 83.0%
Made as	29.92	29.41	28.82	27.51
Made from 32° Bé. (37¼% H_2SO_4)	26.51	26.00	25.41	24.10
Made from 34° Bé. (40% H_2SO_4)	17.20	16.69	16.10	14.79
Made from 41.4° Bé. (50% H_2SO_4)				

Case II.		
Tons water evaporated to make 20 tons acid "98% equivalent."		
	C 93.3%	D 89.1%
Made as	31.59	30.59
Made from 32° Bé. (37¼% H_2SO_4)	27.99	26.99
Made from 34° Bé. (40% H_2SO_4)	18.19	17.19
Made from 41.4° Bé. (50% H_2SO_4)		

Gilchrist points out that, "As separated acid cannot be satisfactorily concentrated to a strength of either 98.0 or 95.1 per cent, it is impossible to operate according to either Case II-A or II-B. Even consistent concentration to a strength of 93.3 per cent (Case II-C) is very difficult, so fortification of concentrated restored acid with purchased acid to an average strength of 98 per cent is practically impossible unless an excessive ratio of purchased acid is used, which means either that the cyclic efficiency is



Courtesy, Atlantic Refining Co. and Chemical Construction Corp.

FIGURE 9. Two "Chemico" Sulfuric Acid Contact Plants.
Daily Capacity of Each, 50 tons of 98% Acid.

less than 66 $\frac{2}{3}$ per cent or that the quantity of acid in the cycle is continually increased, either of which proceedings is economically undesirable.*

"The savings in the cost of restoring acid by concentrating to a lower strength and fortifying in a contact plant can be developed from consideration of the relative amounts of water to be removed in the concentration. This also varies with the original strength of the separated acid, and in Table 26 is shown the quantity of water removed from various strengths

* In actual practice a small amount of water will enter the contact acid plant from the moisture in the air used in burning the sulfur, so that the required strength of the restored acid to be fortified in the contact plant will be slightly above the theoretical figures shown for Cases I-D and II-D.

of separated acid to produce the quantities and strengths of restored acid required by the various cases in Table 25. To simplify the comparison, a constant concentration yield of 100 per cent has been assumed; actually the yield would not be over 95 per cent in the most favorable cases and would decrease as the strength of the restored acid increases, resulting in even greater savings when concentrating to the lower strengths.

"As direct concentrating costs, such as fuel, power, etc., are practically proportional to the water evaporated, it is obvious that these costs per ton '93 per cent equivalent' would average about $12\frac{1}{2}$ per cent less when concentrating to 83 per cent strength than when concentrating to 93 per cent strength. In addition, repairs and upkeep are considerably less and plant capacity is considerably greater when concentrating to the lower strengths, so that the total costs are about 20 per cent lower when concentrating only to 83 per cent strength.

"As restored acid constitutes two-thirds of the total acid used in the cycle, it is obvious that the use of a contact plant at a refinery results in a reduction in acid costs, even if there were no saving in the cost of the fresh acid manufactured in the contact plant compared with the delivered cost of purchased acid. Except under very unusual circumstances, there will be a saving in the fresh acid cost also, so that the refinery with complete acid manufacturing and restoring plant operates its acid cycle much more economically than the refinery which purchases its make-up acid."

In this connection, one refinery is producing fuming sulfuric acid from hydrogen sulfide and adding it to the recovered weak, partly concentrated, sulfuric acid, producing thereby a "black acid" of 98 per cent concentration.¹⁷ Further comments on converting refinery hydrogen sulfide into sulfuric acid are made later in this chapter.

Refineries having complete acid equipment set aside one part of the refinery for the acid section, which, as seen from the foregoing, consists of separating, concentrating, and contact units.

ACID FROM THE HYDROLYSIS OF ACID SLUDGE AS A TREATING AGENT

The acid recovered in the above operations is black. If its separation from the sludge has been properly handled, it is as efficient as fresh acid for treating oils. The recovered acid, though black in color, often has better decolorizing power for light oils than fresh acid of the same strength (ratio of acid content to water content must be considered when discussing the "strength" of recovered acid). This observation has been confirmed by the authors. It has been reported also that the acid recovered from sludge produced by the treatment of vaseline, when reconcentrated and fortified with fuming acid to 93 per cent strength, is a better treating agent for color than fresh acid.^{36, 55}

In general, the extensive re-use of the acid by the large, efficient refineries of the country indicates that it is successfully utilized, and the many reports from these refineries confirm this conclusion. It is possible to determine on a laboratory scale whether any given sludge can be successfully handled and the acid recovered.

LABORATORY CONTROL FOR SEPARATION AND CONCENTRATION OPERATIONS

Separation of Acid from Acid Sludge

Laboratory control tests for the separation of acid from acid sludge give excellent data, but the results require intelligent interpretation. Valuable information may be obtained on the optimum degree of dilution of the sludge, time of heating, and the temperature by placing samples of the diluted sludge in four-ounce bottles and heating them in the following manner. The bottles with loose-fitting glass stoppers are placed upright in bombs made of two-inch iron pipe, eight inches long, capped at both ends, and lead-lined except for the top. Water is poured around the bottles in the bombs to about half their height to prevent the water from distilling from the dilute acid during the subsequent heating; a partial equilibrium is set up between the aqueous tension of the water outside the bottles and the water of the dilute acid during the process of heating. There is a tendency for the acid to become dilute, but practice has shown that the change is negligible. When the top cap is securely applied, the bomb is heated for the chosen time (*e.g.*, two hours) in an electric or other suitable oven or in an oil bath, the temperature of which can be regulated so as to vary not more than 5 to 10° F. At relatively high temperatures, the oil layer in the bottles may become coke-like, whereas it would not do so in the large-scale retort, for here it would be removed or skimmed from the acid layer as fast as it formed and not be subjected to the prolonged heating. After heating, the bottles should be allowed to settle 10 to 24 hours before the content of acid and carbon is determined in the separated acid so that the data will compare with refinery operations.

The total carbon in the weak or separated acid is taken as an approximate measure of the organic matter still in the acid. The weak acid can usually be concentrated satisfactorily if its carbon content is not over about five per cent, based on the actual sulfuric acid in the acid solution.

Experience has shown that in the continued use and recovery of sulfuric acid, the amount of carbon does not accumulate in the acid but reaches an equilibrium after the second or third recovery.

Determination of Content of Organic Matter in Separated Acid

The content of organic matter is estimated by warming a small sample of the separated acid with potassium dichromate and pure concentrated sulfuric acid, and either determining the dichromate reduced by the organic matter or the amount of carbon dioxide evolved from the oxidation.

Determination of Acid Content in Acid Sludge and Separated Acid

The acid content of the acid sludge can be determined by adding a 0.5 gram sample of acid sludge to about 50 cc. of water (the Lunge pipette is suitable for weighing) and titrating with 0.2*N* solution of sodium hydroxide, using methyl orange indicator. In neutralizing acid sludge with caustic soda, emulsions are likely to occur, but they break most readily at the neutral point or within the range of hydrogen-ion concentration of pH 6.4 to 7.6.

A very simple procedure is to weigh a little less than a gram of the acid sludge into an Erlenmeyer flask, add 10 to 20 cc. of carbon tetrachloride (neutral to methyl orange), 25 to 50 cc. of water, and titrate with the alkali, methyl orange being used as indicator. The heavy carbon tetrachloride carries the carbonaceous matter to the bottom of the flask, and the color changes in the indicator are more easily observed. It is usually necessary to add more of the indicator as the titration progresses.

The acid content of the sludge can also be determined by adding a small amount of the sludge to 10 to 15 cc. of acetone in a separatory funnel, agitating the mixture for a few minutes, adding 20 to 30 cc. of water, withdrawing an aliquot portion of the water, and testing it with a hydrogen-ion concentration apparatus.¹² Other methods are described, which can be used for the analysis of the acid sludge and recovered acid.²

Gravity determinations of the sludge acid, particularly of strong acids, are somewhat unreliable because of the presence of carbonaceous material and of salts of sodium and iron.

DIRECT PRODUCTION OF FRESH CONCENTRATED OR FUMING SULFURIC ACID FROM ACID SLUDGE

In recent years a process has been developed by the Chemical Construction Corporation for reconvertng the acid of the acid sludge into pure sulfuric acid of any desired concentration, up to and including fuming acid containing 20 per cent sulfur trioxide (104.5 per cent H₂SO₄ equivalent). Five different oil companies are now using the process. The capacities of these installations vary from 20 to over 100 tons of 100 per cent sulfuric acid per day; the total capacity of the five installations is 320 tons, approximately 270 tons of which consists of acid produced

from acid sludge. The remainder of the 320 tons is produced from hydrogen sulfide and elemental sulfur, or its equivalent. The fifth plant was completed late in 1940 for the Standard Oil Company of New Jersey at the Bayway Refinery near Linden, New Jersey. It has a capacity of 100 tons of acid per day, 75 of which is produced from acid sludge.

In this new recovery process, acid sludge or mixtures of acid sludges undiluted with water are continuously pumped into a rotating kiln internally heated to about 500-550° F. At this temperature the sulfuric acid in the sludge is reduced practically quantitatively to sulfur dioxide by the chemically reactive organic matter of the sludge. Except for a small amount of light oils and fixed hydrocarbon gases that are expelled from the kiln with the sulfur dioxide, all of the organic matter is converted to an acid-free, granular, or pulverizable coke. A small amount of carbon dioxide is expelled, but no hydrogen sulfide, and practically no sulfur trioxide or sulfuric acid. Hydrogen sulfide could not exist because the hot sulfur dioxide would react with it and liberate elemental sulfur.

The kiln in which the sludge is decomposed and all the purification equipment leading up to the contact chambers are maintained under a vacuum of two to six inches of water equivalent. The slight vacuum prevents loss of sulfur dioxide and the escape of malodorous gases. The small amount of air which is drawn into the apparatus is not objectionable since much more air must later be added for the combustion in a secondary kiln of any fixed hydrocarbon gases accompanying the sulfur dioxide, as well as to supply ample oxygen for the oxidation of the sulfur dioxide in the contact chambers.

The sulfur dioxide is freed of moisture, oil, dust, combustible vapors, etc., and is then, with the further addition of the proper amount of air, passed through a catalytic contact mass and converted into acid.*

The quantity of sulfur dioxide expelled from acid sludge is surprisingly high; for many samples of sludge, it is about 93 to 94 per cent of the theoretical amount in the original acid used in treating the oil.⁸⁵ The yield also corresponds closely to the total amount calculated from the acid and the sulfur dioxide in the acid sludge. In practical operation about 90 per cent of this sulfur dioxide, which is evolved, is converted into sulfuric acid. Consequently about 80 per cent of the acid used in treating the oil is regenerated as fresh acid. The lost acid is replaced by burning in the equipment the necessary amount of elemental sulfur or, preferably, hydrogen sulfide, and uniting the resulting sulfur dioxide with that expelled from the acid sludge.

The quantity of acid in the sludge may vary widely and yet give a

* For general methods of manufacturing sulfuric acid, the reader should consult the numerous standard works, especially the publication by Fairlie.⁸⁸

granular or friable coke. The coke is continuously discharged from the kiln; it has a relatively high percentage of sulfur and is commonly used for fuel only. In the latest plants, part of the coke is used as fuel for generating heat to decompose the acid sludge. The coke is first heated by partial combustion to incandescence (about 1600° F.) in a separate kiln and, while glowing, is ingeniously introduced into the sludge conversion kiln along with the acid sludge. This procedure not only utilizes the coke but produces sulfur dioxide of 50 to 70 per cent concentration. The rich sulfur dioxide, undiluted with combustion gases, is more economically purified. In all cases, however, the concentration of the sulfur dioxide is sufficiently high for economical conversion into acid.

The coke itself is free from sulfuric acid but, as noted above, contains a high percentage of sulfur, usually about five to eight per cent. The sulfur in the coke doubtless comes from the sulfur-bearing hydrocarbons extracted from the oil by the acid and from some of the sulfuric acid itself.

Table 27. Recoverable Acid, Distribution of Acid, and Sulfur Balance from Laboratory Acid Sludges.*

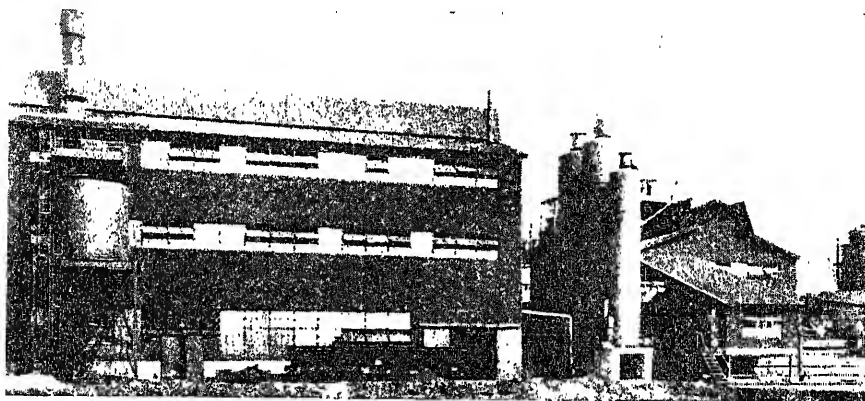
	Kerosene	Cracked Gasoline Refinery A	Refinery B
1. Actual H_2SO_4 used in treating oil (g)	34.38	17.19	16.97
2. Acid sludge produced (g)	49.11	32.10	30.00
3. Coke produced (g)	11.72	8.88	7.55
4. Sulfur in coke (%)	12.63	6.84	8.90
5. Original H_2SO_4 found in acid sludge by alkali titration (%)	96.66	95.26	93.72
6. Original H_2SO_4 expelled from heated sludge as SO_2 (%)	93.95	93.83	93.22
7. Partial accounting for original H_2SO_4 used: Original H_2SO_4 as SO_2 in vapor in agitator used to treat oil and in acid oil (%)	0.12	0.14	1.20
Original H_2SO_4 in acid oil (%)	0.08	0.44	0.20
Original H_2SO_4 expelled from heated sludge as H_2SO_4 (%)	0.25	0.36	0.32
Original H_2SO_4 expelled from heated sludge as SO_2 (%)	93.95	93.83	93.22
Total Original H_2SO_4 accounted for (%)	94.40	94.77	94.94
8. Sulfur Balance:			
Total sulfur in original H_2SO_4 plus sulfur removed from oil (g)	12.295	5.898	6.107
Total sulfur found in 4 and 7 above (g)	12.135	5.951	5.928
Sulfur found/sulfur known (%)	98.70	100.90	97.10

* The oils were treated at normal temperatures; the kerosene was treated in the ratio of 20 lbs. of 94.2% sulfuric acid per bbl., cracked gasoline A with 14 lbs. of 93.3% acid per bbl., and cracked gasoline B with 14 lbs. of 94.2% acid per bbl.

An investigation by Stagner⁸⁵ on some samples of acid sludge produced in the laboratory (see Table 27) shows that the quantity of sulfur extracted from the oil under acid treatment is insufficient to account for all the sulfur in the coke, and that about five per cent of the sulfur in the

sulfuric acid used in treating the oil is not otherwise accounted for. This five per cent portion of the sulfuric acid may possibly be reduced by the organic matter to elemental sulfur or to hydrogen sulfide; the latter would be decomposed by the sulfur dioxide, and the sulfur released as elemental sulfur.

It is not definitely known whether the sulfur in the coke is combined with the carbon or merely strongly adsorbed by it. Considerable evidence exists for both theories. None of the sulfur can be extracted from the coke by carbon disulfide, in which sulfur is easily soluble. Taylor,⁸⁸ in various investigations, has examined a residue remaining after heating elemental sulfur with hydrocarbons and has concluded that the sulfur is most likely in true combination with the carbon.



Courtesy, Atlantic Refining Co.

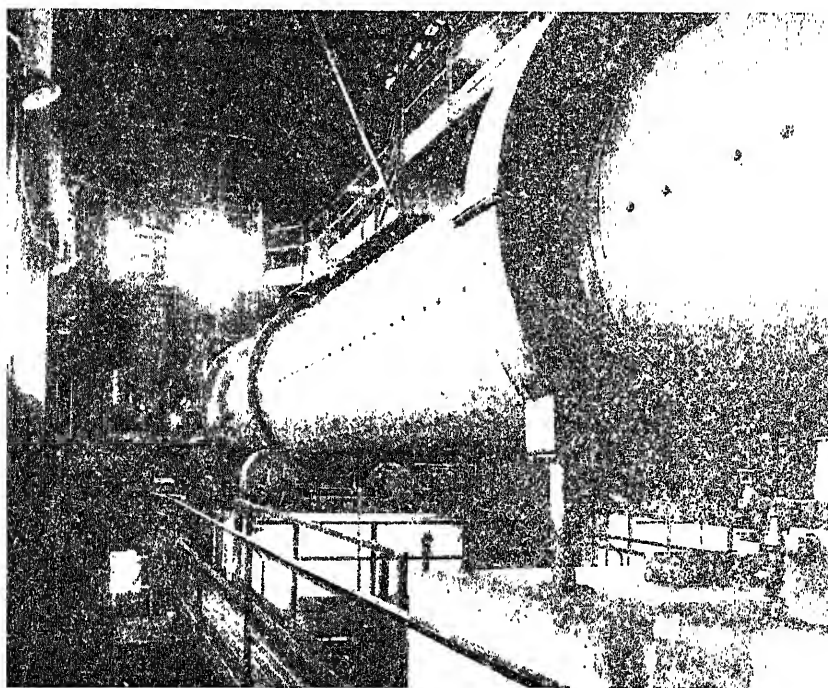
FIGURE 10. The "Chemico" Sludge Conversion-Contact Acid Plant of the Atlantic Refining Co. at Philadelphia.

This process of manufacturing acid from acid sludge was developed by Hechenbleikner and associates; it has been reported in detail in the various patents⁴⁴ and in publications by Spangler,⁸² Oliver and Spangler,⁶⁵ and Hart.⁴³

Hart,⁴³ of the Atlantic Refining Company, has described the construction and operation of an acid-sludge conversion plant, built in 1938; the accompanying photographs of the plant were submitted by Hart through the courtesy of the Atlantic Refining Company. This plant has capacity to handle the acid sludge from the daily use of 65 tons of acid and has auxiliary equipment to convert sufficient hydrogen sulfide into sulfuric acid to replace the acid lost in oil treatment and regeneration. The hydrogen sulfide is a waste product extracted from the gases from the cracking plants.

Hart reports that an average of 89 to 90 per cent of the acid actual in the sludge is converted into acid; the concentration of the regenerate acid is from 98 to 104.5 per cent; the color is practically water white; and the acid is satisfactory in every respect. Provision has also been made for diluting the acid to any desired strength.

The Atlantic Refining Company's sludge kiln is heated internally by the continuous addition of fuel gas and some of the by-product coke previously heated to incandescence in a separate kiln.



Courtesy, Atlantic Refining Co.

FIGURE 11. "Chemico" Acid Sludge Conversion Unit.

The yields of acid sludges from the laboratory treatment of kerosene and cracked naphtha with sulfuric acid and the yields of products formed by decomposing the sludges at about 500° F. were investigated by Stagner.⁸⁵ Table 27 shows the data and an accounting of the sulfur of the acid and of the oil. When the sludges were heated, 93 to 94 per cent of the original acid was recovered as sulfur dioxide.

Table 28 gives yields of products from heating typical California petroleum acid sludges.⁸⁵

Table 28. Sulfur Dioxide from Refinery Acid Sludges Heated to 540° F. (282° C.).

Kind of Sludge	H ₂ SO ₄ Content of Sludge Determined by:			Other Products Based on Weight of Sludge		
	Alkali Titration %	SO ₂ Evolution Iodine %	BaCl ₂ %	Coke %	Oil %	Water %
Gasoline and kerosene:						
Gasoline, straight-run	61.50	61.90	21.3	10	25
Gasoline, cracked (refinery B)	47.08	46.71	46.91	...	10	25
Gasoline, cracked (refinery A)	43.30	45.05	32.6	10	20
Kerosene	45.50	47.90	...	39	10	15
Kerosene sludge and cracked gasoline sludge, mixed 1:4	48.93	52.68	5	25
Lubricating sludge:						
Refinery A ^a	26.85	16.83	57	1	25
Refinery A	38.50	28.00	2	20
Refinery C	23.40	20.30	2	10
Laboratory ^b	37.20	34.00	48.5	2	10

^a This sludge was so hard that the sample had to be cut from it with a knife.

^b California lubricating stock, medium viscosity, treated with 30 pounds of 98 per cent acid per barrel with air agitation for 45 minutes.

The heavy lubricating acid sludges, if relatively rich in carbonaceous material and poor in acid, leave a residue not sufficiently brittle to be powdered; but when the sludge is first mixed with a light oil acid sludge, the resulting coke is easily pulverized.

The percentage of coke available from the sludge is dependent on the nature of the oil and the strength and amount of the acid used in treating the oil. From cracked gasoline and kerosene the yield is usually about 25 per cent of the weight of the sludge, or about 45 to 50 per cent of the weight of the acid used in treating the oil.

The amounts of oil and water distilled from the sludge are also variable. The last two columns of Table 28 show approximate yields of these two products. The water comes from the small amount of water of dilution in the original acid, from the reduced acid, and from the oxidation of the hydrocarbons by the acid.

HYDROGEN SULFIDE IN REFINERY CRACKED GASES; EXTRACTION AND CONVERSION INTO SULFURIC ACID

Because of the more intensive cracking operations, the trend in refining is toward a greater production of hydrogen sulfide in comparison with the acid consumption. Consequently several of the large refiners, as in the case of the plant described above by Hart, now have complete sulfuric acid plants for manufacturing all their own acid, the acid sludge from the acid refining operations and the hydrogen sulfide from the cracking plants supplying all the sulfur needed. The gases from petroleum oils relatively rich in sulfur contain about two to six per cent by volume of hydrogen sulfide. Since a large refinery commonly may produce 15,000,000 to

20,000,000 cu. ft. of gas per day, it thus has a potential yield of 45 to over 100 tons of 100 per cent sulfuric acid from the hydrogen sulfide alone.

Efficient methods have been developed for recovering the hydrogen sulfide in a practically pure state, whether the object of recovery is the manufacture of sulfuric acid or purification of the hydrocarbon vapors. These processes consist essentially in passing the sour gases in an upward direction through a baffled absorption tower countercurrent to a descending stream of a special alkaline solution. The purified, or sweet, gases are discharged at the top of the tower; the fouled alkaline solution is discharged from the bottom; and the hydrogen sulfide is expelled by boiling the solution in a separate "actifier" tower. From the actifier tower, the alkaline solution is cooled and returned to the top of the absorption tower for another cycle of operation. Heat exchangers and exhaust steam are employed.

The alkaline solution must possess the property of extracting the hydrogen sulfide in the absorption tower and of releasing it when heated in the actifier tower. The solution must, therefore, not hold the hydrogen sulfide too tenaciously; otherwise it cannot be reactivated economically. For example, a solution of caustic soda could not be used economically for, although it would absorb the hydrogen sulfide most energetically in a short time, it would soon become saturated; and because of its relatively stable combination with the hydrogen sulfide, it could not be reactivated without the use of a prohibitive amount of steam.

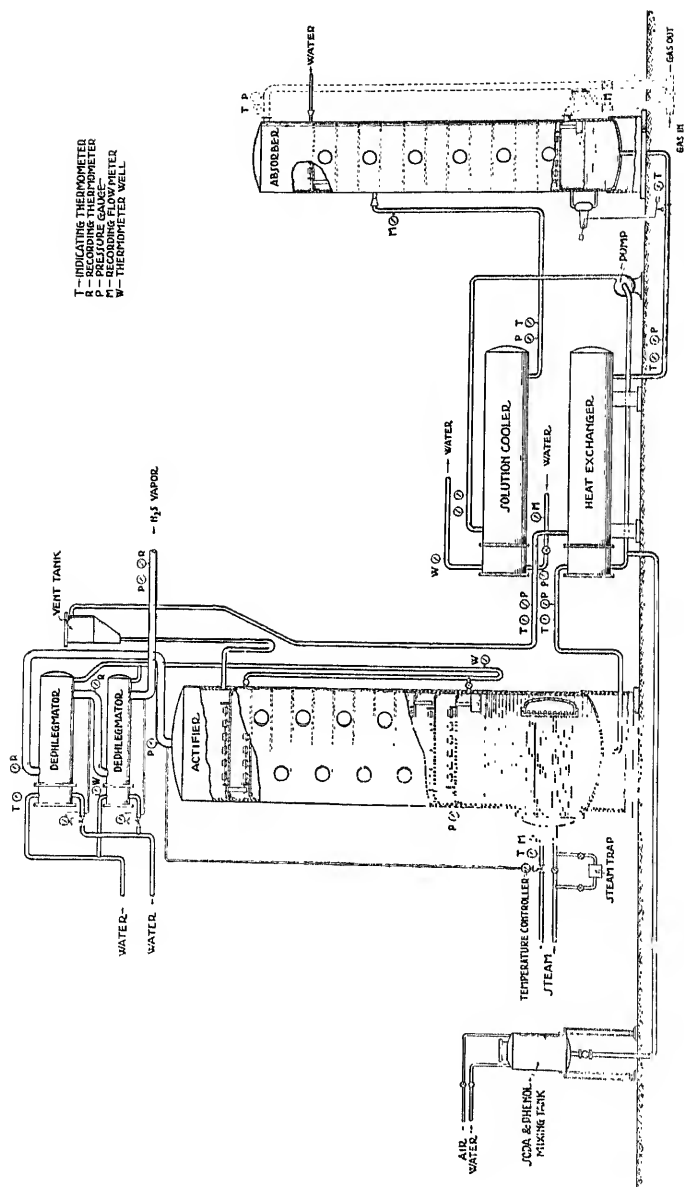
More efficient absorption occurs at normal than at elevated temperatures; and when the gases of the refinery are at normal temperatures, the hydrogen sulfide can be most economically isolated by an absorption solution which will not require too much heat for activation. However, if it is necessary to purify hot vapors, the absorption medium must form a sufficiently stable combination with the hydrogen sulfide to extract it, even though the cost of reactivation is greater.

Three commercial processes for recovering hydrogen sulfide are in successful and extensive use in the oil refineries in this country. They are

- (1) The Koppers Company; solution of sodium phenolate.
- (2) Girdler Corporation; solution of organic bases, such as ethanamines.
- (3) Shell Development Company; solution of tripotassium phosphate.

The Koppers Company Sodium Phenolate Process

The first hot activation plant of the Koppers Company was built in 1936 at the El Segundo Refinery of the Standard Oil Company of California. The plant and its operation have been described by Craige and Brown,¹⁷ and this plant and other similar plants have been described



Courtesy, Koppers Company.

FIGURE 12. Flow Diagram of Single-stage Phenolate Process.

Carvlin,¹⁰ Powell,^{71, 72} Denig and Powell,²² and in patents.⁷⁷ A typical sodium phenolate plant is shown in Figure 12.

The El Segundo plant at full capacity handles 16,000,000 cu. ft. of gas per day; the gas contains from 4 to 6 per cent by volume of hydrogen sulfide; and the daily production of sulfur with full capacity operation a relatively sour gas amounts to 35 tons.

The hydrogen sulfide is catalytically converted into sulfur trioxide and strong sulfuric acid and added to the acid restored from acid sludge by hydrolysis and partial reconcentration, the acid recovery system having already been in operation before the gas purification system was added. These two sources of acid are ample for the refinery.

Craze and Brown point out that the sulfur content of the crude oil used for cracking varies from 0.5 per cent to 2.5 per cent, and consequently the sulfur content of the cracked gases and naphthas varies somewhat in the same order. When more acid is needed for desulfurizing the naphtha, it is available from the greater amount of hydrogen sulfide, a close balance thus being automatically established. The purity of the isolated hydrogen sulfide is from 95 to 99 per cent; and the desulfurization of the cracked gases, as operated for the sulfuric acid manufacture, is from 94 to 97 per cent, the percentage of the desulfurization being controlled by the completeness of the reactivation of the phenolate solution and the rate of circulation of the phenolate solution, both of which are controllable factors within the capacity of the equipment. The percentage desulfurization thus an economic balance between the increased recovery of hydrogen sulfide and the increased cost for steam and power.

Further information on the extent of the activation and circulation of the sodium phenolate is supplied by Powell,⁷² who found that in a single-stage phenolate plant, about 3.5 pounds of steam per pound of hydrogen sulfide removed 90 per cent of the hydrogen sulfide, and 12 pounds of steam would remove 99.9 per cent; but in place of a single-stage unit, if the latter, it would be desirable to employ a two-stage unit, for then steam consumption would be only about 3.5 pounds per pound of hydrogen sulfide to effect the 99.9 per cent purification of the gas.

The Girdler Corporation Process for Hydrogen Sulfide Recovery

The Girdler Process uses solution of certain organic amines, such as the ethanolamines, for the extraction of hydrogen sulfide. Usually the solutions consist of a rather high concentration of the amines dissolved in water. The process is also used in the recovery of carbon dioxide from cracked gases; several plants are in operation for this purpose.⁵⁸

This process can be operated for desulfurizing gases at a temperature

as high as 160° F., which is sometimes necessary in the purification of refinery gases that are to be polymerized into gasoline.

The units and their operations in desulfurizing gases have been described in the literature.^{9, 96}

Shell Development Company Tripotassium Phosphate Process

The Shell Development Company uses an aqueous solution of tripotassium phosphate, 40 to 50 per cent solution, in its hot activation process. Weaker solutions of the potassium phosphate strip hydrogen sulfide from gases more effectively than strong solutions, but cannot be reactivated economically. To some extent advantage can be taken of the more efficient absorbing power of the weak solution by diluting a portion of the strong solution with water condensed from the steam expelled with the hydrogen sulfide, and then using the resulting weak solution in a second-stage scrubbing of the partly purified gases. The fouled weak solution then is blended with the strong solution, and the whole reactivated. The tripotassium phosphate solution holds the hydrogen sulfide rather tenaciously, and for that reason can be used to purify gases at as high a temperature as 200° F. The process has been described very completely in trade journals and in patents.⁵²

I. G. Alkacid Process

This hot activation process, recently developed by I. G. Farbenindustrie and reported to be in use in Germany but not in America, employs as absorption liquid an aqueous solution of salts of certain weak organic acids, such as the aminosulfoacids.³ Hydrogen sulfide is absorbed at normal temperatures from the gases and expelled from the absorbent medium in the actifier tower at about 215° F.

Other methods are in use for freeing gases from hydrogen sulfide, although the hydrogen sulfide cannot be converted into acid so economically as the pure hydrogen sulfide isolated in the hot activation processes described above.

The Iron Oxide Method is the oldest and is still in extensive use. It consists of huge boxes of iron hydroxide dispersed on shavings, or the like; the sour gas is passed through this porous material. Iron sulfide is formed and is converted into the hydroxide and elemental sulfur by oxidation with moist air. The regeneration and purification operate simultaneously if a small amount of air is first added to the impure gas. Eventually too much sulfur accumulates, and a new charge of hydroxide is provided. This method is now considered to be practical in America only for gases bearing a very small percentage of hydrogen sulfide.

In the Seaboard Process⁸⁰ the sour gas is scrubbed in one tower by a continuous countercurrent solution of soda ash (about 3 per cent strength), and the fouled soda ash solution regenerated in a separate "actifier" tower by a large volume of air at normal temperature. The hydrogen sulfide is expelled with the air, and the actified solution returned to the absorber for further use. Hydrogen sulfide is lost with the air. In a refinery, the air from the actifier can be used to support the combustion of the fuels used in stills and boiler plants, and the hydrogen sulfide thus burned. Over sixty such units are now in use in the United States and Canada alone.⁷²

The Thylox Process, developed by the Koppers Company,^{48, 72} is a continuous liquid purification process yielding elemental sulfur from the hydrogen sulfide. The absorption medium is arsenic trioxide dissolved in aqueous soda ash solution. The chemical reaction between the arsenic and hydrogen sulfide is irreversible; but the arsenic solution is regenerated, and the sulfur released as elemental sulfur, when the aqueous solution (a true solution) is oxidized by air at about 95° F. The sulfur is separated from the arsenic solution, and the latter returned to the absorption tower for another cycle of operation. The elemental sulfur is in a very fine state of division and for that reason has special value as an insecticide for dusting on plants.

A modification of the Thylox Process, without regeneration of the arsenic solution, is used to purify gases having too little hydrogen sulfide (25 grains per 100 cu. ft., or less) to pay for its recovery. The sodium arsenite solution is recirculated in the absorption tower until the arsenic is substantially exhausted and is then discarded for a fresh solution. Natural gas thus treated is considered to be free of hydrogen sulfide, and gives a negative result in the lead acetate test for hydrogen sulfide.

The Ferroox Process employs a soda ash solution with ferric hydroxide in suspension to absorb hydrogen sulfide from gases.⁸⁴ The absorption is efficient; but the elemental sulfur, when liberated in the actifier under air oxidation, is somewhat impure. This process is now in use in only two or three plants in America.

The Nickel Process¹⁸ uses a nickel catalyst in suspension in a solution of sodium carbonate. It operates very similarly to the above Ferroox method although the resulting elemental sulfur is much purer. Several of the Nickel Process units are operating successfully in gas plants in this country.

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Chapter IV

Treatment with Alkaline Reagents

Alkaline reagents are used in refining petroleum products to remove the acidic constituents normally in the oil and those added to it during refining, particularly by sulfuric acid and by substances, such as phenols and sulfur dioxide, used in solvent refining. Sulfuric acid, when used in economical amounts, does not effectively remove such impurities as hydrogen sulfide, organic acids, and mercaptans. Moreover, the acid treatment leaves in the oil deleterious products from the acid itself, *e.g.*, sulfur dioxide, sulfonic acids, alkyl sulfates, etc., which must be removed to improve the initial color and odor of the oil and to insure chemical stability, etc. Although alkaline reagents are generally used to remove these acidic substances, under certain circumstances adsorbent clays are used for the same purpose, a subject discussed in the chapter on Adsorbents.

Although treatment with alkaline reagents or clay always follows acid treatment, the alkaline reagents are sometimes also applied before the acid treatment for reasons discussed below.

During the alkaline treatment, the oil may be in the liquid or in the vapor phase; the alkaline reagent may be in an aqueous or organic solution, especially in alcohol solution; or in a gaseous form, as in the case of ammonia; or in the form of powdered or granular solids. The aqueous solution is most commonly used.

Although the amount of water associated with the alkaline reagent usually has little or no effect on the oil treated, in some cases it does have a very great effect. For example, Brandt and Hougen²¹ show that washing with caustic methanol solution, in which there is no water, or only a little water, gives gasoline treated with weak sulfuric acid greater stability than washing with aqueous caustic soda solution; an anhydrous, or nearly anhydrous, alcoholic solution of potassium hydroxide reacts instantly with elemental sulfur dissolved in gasoline; and an alcoholic solution of sodium hydroxide or potassium hydroxide likewise brings about the instantaneous oxidation of mercaptans in gasoline by elemental sulfur, whereas aqueous solutions are for all practical purposes inert unless a large excess of elemental sulfur is present.

CHEMISTRY OF ALKALINE TREATMENT

The discussion below pertains primarily to sodium hydroxide as the most commonly used alkaline reagent. However, other alkaline substances

must be considered because of their special chemical characteristics or economy of use.

Soaps

The stronger acidic substances of the type of organic acids or phenols are changed by sodium hydroxide or similar alkaline reagents into their respective alkaline salts, which are soluble in water and thereby removed from the oil. The reaction between sodium hydroxide and the organic acidic substances is reversible; the hydrolysis, though noticeable in the water solution, is more apparent when the sodium hydroxide solution is in contact with the oil, in which these organic acids are soluble and the alkali insoluble, the effect being the manifestation of the partition coefficient of the organic acids between the oil and the aqueous solution. It is even possible to extract all the organic acid from sodium soaps by repeated treatment with hydrocarbons.^{58, 74} Because of the hydrolysis it is often more desirable to treat the oil with a very strong solution of sodium hydroxide than with a weak solution;⁷³ but this is not always practical because of other complications, such as severe emulsification and the resulting losses of oil and alkali.

The sodium soaps of organic acids are generally soluble in water, *i.e.*, the partition coefficient is shifted considerably in the direction of water. This shifting is true, however, only for the sodium soaps of low molecular weight acids, which can be relatively easily extracted from the oil by water washings. The oil is washed with water after the sodium hydroxide treatment in order to remove the last traces of alkalies and to leave the oil neutral; traces of alkalies left in the oil may be objectionable, particularly because of the increased ash content of the oil.

The sodium salts of the organic acids are normally decreasingly soluble in water as the ratio of sodium to hydrocarbon in the molecule diminishes. For this reason the sodium salts of organic acids in high-boiling petroleum distillates are often only slightly affected by water washing, and are left in the oil after repeated washings. Moreover, they are highly conducive to formation of emulsions. Such distillates are, therefore, usually neutralized with clay instead of sodium hydroxide or other similar alkaline reagents.

If lime is substituted for sodium hydroxide, the resulting calcium salts are much more soluble in oil than in water; they therefore cannot be washed from the oil with water under normal plant conditions. The resulting product will have a high ash content unless another finishing operation is employed.

If water hydrolysis of the sodium soaps were the only factor involved it would be theoretically possible to apply successive extractions with increasing strengths of alkali and recover first the stronger acids with small

molecular weights and certain phenols, and later the weaker acids with larger molecular weights. Some success has been attained in this direction;²⁵ but, as observed above, the high degree of solubility of the organic acids in the oil prevents the extraction from being so simple. It is easier first to extract the acidic substances from the oil by using the strongest possible alkali solution and then fractionally precipitate these same acids from the aqueous solution, if their isolation is desired, by gradual or partial acidification. Weak acids, such as carbon dioxide, hydrogen sulfide, etc., are suitable for the acidification. Cresylic acids and other phenols can be recovered from cracked distillates in this manner.²⁷

Experiments indicate that cracked distillates may contain as much as 0.01 per cent by volume of phenols.¹¹⁴ Field, Dempster, and Tilson⁴⁸ present an extended report of their investigation on the phenolic compounds occurring in cracked naphtha. They isolate the individual compounds and compare their insecticidal values with phenolic compounds from coal-tar products. They also supply a historical review of the literature on the nature and occurrence of the phenolic substances in petroleum.

Hydrogen Sulfide Removal with Alkaline Reagents

Of the naturally occurring sulfur compounds in oil, only hydrogen sulfide and some of the lower molecular weight mercaptans and the thiophenols are removed by an aqueous solution of sodium hydroxide. For the removal of hydrogen sulfide, caustic soda solution is widely used. Hydrogen sulfide is usually present in the crude oil, and additional quantities may be formed on distillation because of the partial decomposition of the less stable sulfur compounds. It may be advisable, when practicable, to remove hydrogen sulfide from a light oil before distillation so as to prevent its being oxidized to elemental sulfur, which is more difficult to remove than the original hydrogen sulfide. The distillates may be collected in receivers containing sodium hydroxide solutions to prevent oxidation of the hydrogen sulfide to elemental sulfur by the small quantities of free oxygen in the system. If hydrogen sulfide and a small amount of elemental sulfur are in an oil, they can be removed simultaneously by treatment of the oil with a very small quantity of strong sodium hydroxide.³¹ The sodium or other similar hydroxide reacts with the hydrogen sulfide, forming the respective sulfide; this sulfide further reacts with the elemental sulfur, forming polysulfides, which are soluble in water and removed from the oil. A strong aqueous solution of sodium or potassium sulfide, and especially an alcoholic solution of the sulfides, absorbs elemental sulfur from oils.

In the course of distillation, hydrogen sulfide is sometimes removed by passing the oil vapors through extremely dilute solutions of caustic soda, concentrations of about 0.2 per cent being suitable. The weak solutions

are claimed to give better utilization of caustic than stronger solutions.¹⁰⁷ However, the use of these weak solutions necessitates the handling of large volumes of liquids, volumes equal to or greater than the oil being treated.

Extraction of Mercaptans with Alkaline Reagents

Mercaptans tend to form mercaptides with the alkali metals when the oil distillates are contacted with the alkaline reagents. The reaction is reversible, as in the case of the weak organic acids and phenols. The strength of the caustic solution is important in effecting the maximum removal of mercaptans. In his study of the chemistry of mercaptans in petroleum products, Borgstrom¹⁸ finds that the maximum removal of mercaptans is effected by alkali solutions of about 2-molar concentration (7 to 8 per cent) and that the secondary mercaptans are more difficult to remove than the primary. Although the removal of mercaptans by the aqueous sodium hydroxide solution is far from complete except for the lowest members of the series, Vesselovsky and Kalichevsky¹²¹ demonstrated that mercaptans can be removed quantitatively by the anhydrous reagent. However, the reaction time is very great, and it is probable that the elimination in the long period of agitation comes from oxidation to alkyl disulfides or combination with other constituents of the oil through the influence of the alkali rather than from extraction by the alkali.

As noted in Chapter II, combined sulfur in gasoline has little or no effect on the octane rating of the gasoline, but it decreases the efficiency of tetraethyl lead if the latter is added to the gasoline. Caustic soda solutions when applied to gasoline in a countercurrent manner are efficient in removing hydrogen sulfide and the lighter mercaptans. Ridgway¹⁰² gives an interesting survey and experimental data on the removal of the mercaptans. The equilibrium constant (K) which represents the quotient of the concentration of the mercaptans in the caustic phase divided by the concentration of mercaptans in the gasoline phase has been approximated in Table 29.

Table 29. Equilibrium Constants for Various Aliphatic Mercaptans in Gasoline and Sodium Hydroxide Solutions of 16° B_c.

Mercaptan	Equilibrium Constant (K)
Methyl	200
Ethyl	80
Propyl	20
Butyl	4
Amyl	1

The equilibrium constants of the table depend upon the strength of the caustic solution and the temperature; they therefore should be considered as relative and not absolute values. They clearly indicate that only

the methyl and ethyl mercaptans of this series of mercaptans can be removed easily from the oil by the caustic solutions. (Table 30 in a different investigation also shows the increasing resistance to caustic extraction offered by the mercaptans of increasing molecular weight in the series.)

Figures 13 and 14, taken from the article by Ridgway,¹⁰² show respectively the influence of volume and strength of caustic and influence of multi-stage washing on mercaptan removal from gasoline. The gasoline originally contained 0.05 per cent mercaptan sulfur.

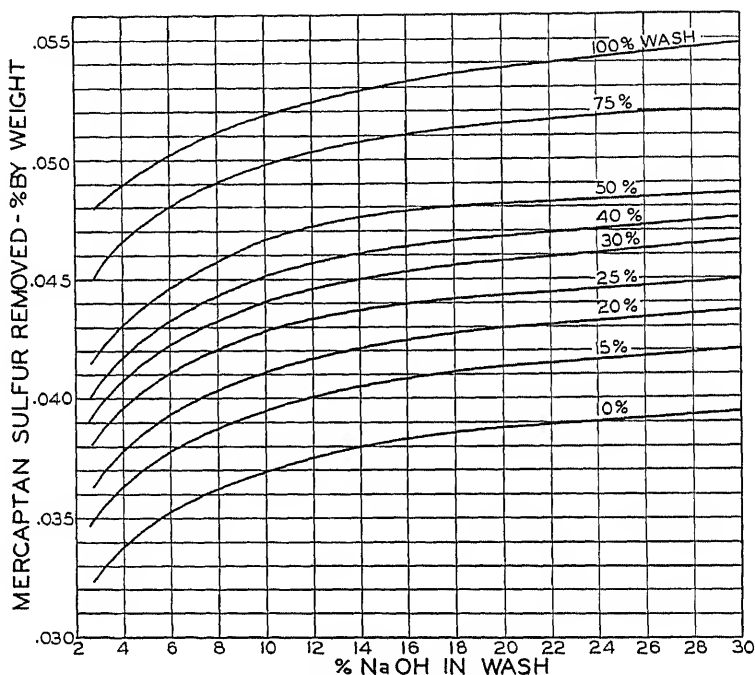


FIGURE 13. Influence of Caustic Strength and Volume upon Mercaptan Sulfur Removal.

Ridgway makes the following general conclusions:

"All of the information available at the present time indicates an appreciable saving in tetraethyl lead can be realized by the removal of sulfur compounds. It is also apparent that caustic soda can be used for the extraction of mercaptans and that the volume, concentration, and temperature of the caustic soda are very important. The amount of mercaptan sulfur that can be removed and the effect of its removal upon the tetraethyl lead response of the gasoline depends upon the type of mercaptans present and the nature of the motor fuel. Hence, the economic advantage

of caustic washing gasolines must be determined for each individual stock by evaluating the influence of the above mentioned factors. In closing, it might be well to point out that it is most difficult, if not impossible, to conduct batch-treating operations without experiencing a loss of light ends, so that a serious error is introduced when an effort is made to determine comparative tetraethyl lead responses of gasolines so treated. Our experience indicates that a closed continuous countercurrent system must be used for this work."

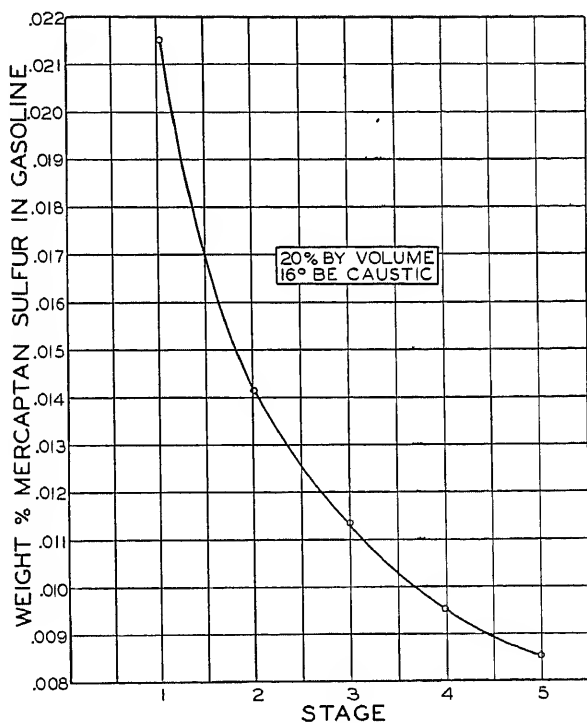


FIGURE 14. Influence of Multi-stage Washing on Mercaptan Content of Caustic-Washed Gasoline.

In a later publication by Ridgway and associates,⁶² it was shown that the sodium hydroxide solution used in scrubbing certain cracked gasoline absorbed a high percentage of mercaptans having aromatic hydrocarbon radicals which could not be expelled from the alkali economically by boiling. The mercaptans were almost wholly ortho-thiocresols, but there were small amounts of para-thiocresol and thiophenol. The ortho-thiocresol is a fairly strong acid, almost as strong as acetic acid, and it is fairly soluble in water, a property which greatly facilitates its extraction by the alkali.

solution. The constants for the extraction of the thiophenols with caustic soda solution would be very different from those of the mercaptans having aliphatic radicals noted above.

A review is also made in this second publication⁶² of the carboxylic acids, formic, acetic, propionic, butyric, palmitic, stearic, etc., that have been found in petroleum or petroleum products. Such acids would be extracted by caustic soda solution but could not then be expelled economically from the caustic soda solution by heating.

Dunstan⁴² has reported the percentages of hydrogen sulfide and mercaptans removed from naphtha under similar conditions of treatment with sodium hydroxide solution. The low acidity of the higher molecular weight mercaptans and their larger hydrocarbons nuclei become manifest in their low extraction by the caustic soda solution.

Table 30. Extraction of Hydrogen Sulfide and Mercaptans from Naphtha by Caustic Soda Solution.

Substance	B. P. (° F.)	% Removed	B. P. of Corresponding Disulfide (° F.)
H ₂ S	...	100.0	...
Ethyl mercaptan	102	97.1	306
<i>n</i> -Propyl mercaptan	154	88.8	...
Isopropyl mercaptan	138	87.2	347
<i>n</i> -Butyl mercaptan	208	63.2	...
Isobutyl mercaptan	190	62.8	428
Isoamyl mercaptan	244	33.0	...

In many refineries the sour cracked gasoline is subjected to counter-current extraction with aqueous caustic soda solution before the sweetening operation,^{1, 9} a process cheaper than plumbite sweetening. The caustic soda is regenerated by boiling, and re-used; the expelled mercaptans are burned in a furnace. Under normal conditions, about 50 to 60 per cent of the mercaptans are extracted by the caustic soda solution. Since some of the sulfur is removed from the gasoline by the extraction, the finished gasoline is given a higher lead susceptibility than if a sweetening process alone were used which merely converts the mercaptans to the corresponding disulfides. The significance of mercaptan removal and lead susceptibility is discussed in the chapter on Sweetening.

The Yabroff "Solutizer" process, in which chemical reagents are added to the caustic soda solution to increase the solubility of the mercaptans therein, is primarily a sweetening process and is therefore discussed later in the chapter on Sweetening.

Kimball⁷¹ claims that mercaptans are removed by contacting gasoline or kerosene vapors with a strong solution of sodium hydroxide heated to above the condensation temperature of the hydrocarbon vapors but below the boiling point of the alkaline solution. He states that only part of the

mercaptans can be recovered from the sodium hydroxide solution after neutralization with acid and assumes that the remainder has been oxidized to alkyl disulfides by the sodium polysulfides in the sludge. However other factors play an important part, such as oxidation by air, condensation with olefins, etc.

For other information on the use of caustic soda for extracting mercaptans from oil, the reader is referred to the above articles and to some what similar articles by Crary and Holm,³⁴ Borgstrom, Dietz, and Reid,¹ Happel and Robertson,⁶⁰ Meyer,⁸¹ Borgstrom,¹⁸ and Albright.¹

Removal of Acidic Substances Introduced into Oil

The acidic and potentially acidic substances introduced into the oil by the sulfuric acid are likewise removed by the alkalis, but to a variable extent, depending on their nature. Sulfuric acid is readily neutralized by the alkalis and removed without any difficulty in the form of sodium sulfate by the subsequent water wash. Alkyl hydrogen sulfates are strong acids and are easily removed. However, the dialkyl sulfates are hydrolyzed slowly by the alkali solution and therefore may be only partially removed from the oil.

It can be expected that on heating an oil with alkalis and redistilling the gum content will be reduced.¹⁵ Lowering of the gum content after acid or alkali refining and redistillation depends largely on the distillation step; entirely different results may come from improper distillation.

The following is a survey of the effects of sodium hydroxide treatment on oils:

(1) Stabilization against chemical change and sometimes an immediate improvement in color. The discoloration of light oils in storage can often be traced to the development of acidic substances or to the incomplete removal of the acids.²³ Some of the cracked distillates, however, are darkened by the sodium hydroxide treatment. This condition is rare and can usually be prevented by a preliminary water wash or other treatment. Likewise removal of the phenol-like compounds may adversely affect the storage stability, as some of them may act as inhibitors. An indiscriminate use of sodium hydroxide is not justified, and laboratory tests are desirable to establish proper treating limits and modifications in the alkaline treatment and water washings.

(2) Lowering of the distillation end point of acid-treated cracked naphtha because of the removal by the alkali of sulfuric acid esters or because of hydrolysis and then removal of dialkyl sulfuric esters.

(3) Reduction in sulfur content by the removal of all the hydrogen sulfide, some of the mercaptans, and under special conditions of treatment some of the elemental sulfur. Sodium hydroxide has long been used to

improve the odor of oils.⁸³ The effect is due to the removal of traces of hydrogen sulfide, mercaptans, and certain naphthenic acids.

Plant Practice

As stated above, the oil distillate may be treated in the liquid or in the vapor phase with the alkaline reagents; and the reagent may be in solution in water or other solvent, or in a gaseous or a solid state. The discussion below pertains primarily to sodium hydroxide, although for some purposes other alkalis may be used, as noted later in the chapter.

When the oil is treated in the liquid phase, sodium hydroxide is nearly always applied in aqueous solution, and is usually purchased as such, though it can be prepared at the plant by dissolving solid sodium hydroxide in water.

Kauffman⁸⁸ describes methods for preparing the sodium hydroxide solutions in petroleum refineries.

The oil may be washed with sodium hydroxide solution either before or after the acid treatment, or both. If a caustic wash precedes acid treatment, better yields of treated oil are usually obtained, the amount of acid actually consumed is smaller, and the finished oil contains less sulfonation products.¹⁰⁷ The saving in the quantity of acid is explained by the removal of substances from the oil which otherwise react with the acid and increase the acid consumption. However, these advantages should be balanced against the additional cost of the extra neutralization step. Nevertheless, this step cannot always be avoided without inferior results.

The importance of washing light distillates, particularly from cracking stills, with caustic soda solution in the "run-down" lines from the condensers has been emphasized¹⁰⁸ to prevent oxidation of the hydrogen sulfide in such distillates to elemental sulfur. It has also been pointed out that preliminary caustic washing may be beneficial in treating transformer oils⁷⁹ and that caustic washing of kerosene prior to acid and clay treatment may improve the final color.⁶⁶

Although usually a weak sodium hydroxide solution is used for washing the raw distillates, some refineries use a small quantity of strong solution. The latter plan is often desirable to decrease the total volume of liquids handled. Thus Willson,¹²⁶ in describing the operation of one of the refineries in Texas, states that gasoline from the Cross cracking units is treated with 21° Bé. (15 per cent) sodium hydroxide solution before decolorization with acid and clays.

The optimum concentration of the sodium hydroxide solution varies with different distillates; it should be experimentally determined. As already stated, a strong sodium hydroxide solution is more convenient to use for neutralization of all acidic substances than a weak solution; but

because of inevitable losses in emulsification, a 10° to 20° Bé. caustic solution (5 to 15 per cent) is generally more economical.²² A very dilute solution, however, is the subject of an old patent for use on some oils.⁸⁰ Such dilute solutions of about 2° Bé. or less are often applied in refining lubricating oil distillates because they are less conducive to emulsification. Thus lubricating oils may be treated with solutions containing as little as 0.3 to 0.6 per cent sodium hydroxide, preferably warm, prior to water washing.⁸⁷ On the other hand, solutions as strong as 35° Bé. (28 to 29 per cent) are not uncommon.¹⁰⁰

In general, a weak alkaline solution dissolves the soaps without much difficulty and removes them from the oils, whereas a strong alkaline solution may precipitate ("salt out") the soaps as solid products, which are soluble neither in the oil nor in the alkali solution; in the solid form these soaps act as emulsifying agents of the Pickering type and emulsify the oil and aqueous solution. Moreover, when water is added later, a dilute soap solution results, producing its type of emulsification (oil in water).

In treating lubricating oils it is frequently noted that a strong sodium hydroxide solution gives a better "break" than a weak solution. However, almost invariably the strong caustic gives greater emulsification when the oil is subsequently washed with water. During these water washes an interphase emulsion tends to form between the layers of water and oil. This emulsion, or "rag," often increases rather than decreases as more water is added, particularly with oils neutralized with strong caustic solution or with oils subjected to a heavy acid treatment. The water washing is, therefore, discontinued, either when the wash water is neutral to phenolphthalein or when the amount of the "rag" begins to be excessive.

It is possible to apply to the lubricating oils a very small amount of 50 per cent caustic solution to remove the weak naphthenic or other organic acids, provided the oil is further treated with an adsorbent, such as fuller's earth.⁷ The fuller's earth adsorbs all the soaps as effectively as or better than, a wash with water. For this purpose certain clays are far more efficient than others, but it is doubtful whether any is better than finely powdered Florida fuller's earth.

The caustic solution is usually applied to lubricating oils after acid treatment without first washing the acid oil with water because of the formation of emulsions with the water wash.¹⁰⁰ However, the so-called "gas blowing" or "air blowing" of the oil in contact with a little water as described in Chapter II, may be regarded as a water wash.

In treating light petroleum products, the caustic solution is sometime applied immediately after the removal of acid, but it is almost always preferable to wash the oil with small quantities of water before the caustic wash.

Mixtures of fresh and partially spent sodium hydroxide solutions may be used to treat oils, a procedure which in some cases serves to yield color-stable products, particularly if the treating is carried out at elevated temperatures.

The methods of contacting caustic solutions with oil are similar to those described for contacting sulfuric acid with oil, as both treatments consist essentially in bringing two immiscible liquids into close contact. Continuous methods are preferable for light oils, and batch methods for lubricating oils; many standard methods have been published for both.⁸⁶ A special apparatus employing a system of baffles may be convenient for washing oils with hot sodium hydroxide solution.⁹⁵ A method of filtering through mixtures of sodium hydroxide and other alkaline substances has also been described.⁹⁶

The temperatures of treatment with alkali solutions are about the same as those with acid, although at times for certain stocks they are much higher. Approximate temperatures, though subject to wide variations, are given in the chapter on Sulfuric Acid Treatment. High temperatures in the alkali treatment are much less detrimental to the color than in the acid treatment. In treating lubricating oils, it is often possible to heat the oil and alkalis nearly to the boiling point of water without injuring the properties of the oil. The higher temperature is desirable as it causes faster settling. Even such sensitive oils as transformer or turbine oils may withstand the high temperatures for a sufficient length of time to effect good settling.

A patent embracing the significant features of treating naphtha at high temperatures with sodium hydroxide solution was granted in the beginning of the petroleum industry.¹¹² Later this procedure was patented for use on cracked distillates to remove gums and gum-forming substances, the specified temperatures being above 350° F., and the corresponding pressures, to keep the distillates in the liquid phase, being 100 to 150 pounds per square inch.¹⁵ The use of such high temperatures is very uncommon, however, as the pressure equipment is expensive and the benefit derived may not necessarily be proportionate.

The amount of sodium hydroxide applied to the oil is variable. A large excess is expensive; and the final results are usually, but not always, the same as if only a little excess were used. When the caustic soda is applied to the oil, a certain time is required before the chemical reaction is complete. With an unknown oil, it is therefore customary in a batch treatment to add first a quantity of caustic slightly in excess of that shown by the neutralization number of the oil. After a few minutes of agitation, a sample of the oil is tested for alkali with phenolphthalein; if the test is negative, more caustic is added until a sample from the batch is alkaline.

In continuous neutralization of acid-treated light distillates, the use of an indicator consisting of a mixture of methyl red and xylene blue is recommended.⁵⁵ The color is red with excess acid, green when neutral (for pH values of 7.5-9.0), and blue with excess caustic.

The distillation of oils in contact with sodium hydroxide is the subject of many patents.³⁰ The quality of lubricating and other oils is often improved by treatment in this manner,¹²⁵ and corrosion of equipment is greatly reduced.¹¹¹ Such methods are particularly helpful in distilling crude oils containing large quantities of naphthenic acids because the removal of these acids is not always possible by washing even with strong sodium hydroxide solutions, especially because of the emulsification tendencies. In practice the oil and alkali solution are charged directly to the still. The caustic solution may be of any desired strength because the water evaporates when the oil is flashed.

Although the above method is very positive in removing organic acids, it has the disadvantage of leaving soaps in the still residues. These soaps make the residues unsatisfactory for asphalt manufacture and to some extent for use as fuel because of the harmful effect of the alkalies on the brick walls of the furnaces. The removal of these soaps from the heavy asphaltic residues is difficult, although methods of removal are available. Usually, however, such residues are burned as fuel after they are mixed with the proper quantities of other oils to reduce the ash content to practical amounts.

Normally the ash content cannot be removed from the residuum by treatment with dilute sulfuric acid or by other conventional means because of the ensuing emulsions. Recently Scafe¹⁰⁶ developed a practical and economical method for "de-ashing" these residuums and other heavy petroleum products. The method involves treating the residuum at an elevated temperature with molten boric acid, which reacts with the sodium naphthenates. The resulting anhydrous sodium borate is insoluble in the oil and settles out. The boric acid is then regenerated by treating the salt with sulfuric acid and is again ready for use on the residuum.

An old patent recommends distilling the oils in contact with a mixture of sodium hydroxide, hydrated lime, and sodium sulfate.⁵⁴ Distillation in contact with small amounts of oxides, hydroxides, or carbonates of alkalies, or similar compounds of calcium, barium, or aluminum, as well as with sodium ferrite, sodium aluminate, and other salts of amphoteric acids is also patented.³⁰ The distillation may be conducted under vacuum,¹¹⁶ or the oil vapors may be scrubbed in dephlegmators with a solution of sodium hydroxide which contains some dissolved copper oxide.⁹⁷ Another patent specifies the use of sodium hydroxide in cracking crude oils of high sulfur content.⁹⁴ Distillation in contact with alkalies is also helpful for lubricating oils refined with liquid sulfur dioxide.⁴⁹ Various types of apparatus for distilling oils in contact with chemical reagents have been patented.³⁴

It is claimed that certain stocks which are to be cracked yield a more

easily refined gasoline if the stock is first forced at 3 to 6 atmospheres' pressure and at 300 to 400° F. through a caustic soda solution.¹⁰⁹ The benefit would result mainly from the removal of hydrogen sulfide, some of the mercaptans, and elemental sulfur. The acid-treated oil and the alkaline solution may be introduced into the fractionation tower of a still to secure better contact because of the elevated temperature.⁹⁶ The alkali also lessens corrosion of the metal of the column. This method of treatment is sometimes used in the redistillation of acid-treated cracked gasoline or distillates. In this way any sulfur dioxide from the decomposition of sulfonic acids and alkyl sulfates is neutralized. The alkali is likely to cause encrustation on the baffles or other grid work in the tower of hard, resinous material, which must be removed when the efficiency of the tower is lowered. Lime, soda ash, or ammonia may be used to lessen the corrosion of equipment.

The Fleming process⁴⁹ consists in spraying water, or water bearing a small percentage of alkali, into the vapors as they pass from the still or cracking unit through a narrow constriction. The alkali spray cools the vapors (not an efficient cooling process) and also neutralizes the acidic content. Besides water or solutions of sodium carbonate, the basic patents also specify calcium hydroxide, lead acetate, or suspensions of litharge.

Many other processes for treatment of oils in the vapor phase are described in the technical literature and in patent specifications. By treating oil vapors at 650° F. with a mixture of fused sodium and potassium hydroxides, it is reported that in some cases mercaptans are completely removed; but alkyl sulfides are only slightly affected.¹²⁰ In treating oil vapors with sodium hydroxide solution, enough steam is introduced with the oil vapors to keep the concentration of the sodium hydroxide solution constant.¹²⁴

Some desulfurization (elemental sulfur, hydrogen sulfide, mercaptans) may be effected by passing oil vapors through caustic alkalies or oxidizing agents.⁹ A patent specifies the removal of nitrogen compounds from oil by vapor-phase treatment with a porous mass of sodium hydroxide, lime, and sodium sulfate.⁸¹ In another patent it is claimed that an oil may be advantageously cracked by passing the oil vapors through molten sodium hydroxide or nitrate.⁸⁸ Vapors of vapor-phase cracked gasolines are also treated with caustic alkali solution.¹⁰³ The vapor-phase treatment of lubricating oils with caustic alkalies is patented.¹¹⁷

Near the end of Chapter III is reviewed the development of the purification of hydrocarbon gases, especially refinery gases. These are sometimes scrubbed with aqueous caustic soda solution in a practical manner,^{1, 102, 103} provided the gases contain only a small amount of hydrogen sulfide and little or no carbon dioxide.

Emulsions

When an oil, especially if acid-treated, is contacted with a solution of an alkali, emulsions are usually formed because of the resulting sodium

salts of naphthenic, phenolic, and sulfonic acids. The emulsions in light oils do not often give serious trouble; but in heavy distillates, such as lubricating oil distillates, they may be very persistent. Some of these emulsions may appear as semi-solids (gels), so stiff that they can be cut with a knife; emulsions of such type may form in distillates as light as kerosenes.⁵⁸ The stiff emulsions are sometimes formed in sweetening gasoline with the alkaline doctor solution, but here the solid lead sulfide is essentially responsible.

Serious emulsification in the refining of lubricating oils can be lessened, and in some instances avoided, by proper technique. When economically possible, the emulsification is decreased by a preliminary removal of the organic acids, or by the introduction of demulsifying agents into the caustic solution, or, as in the usual practice, by special precautions in treating with caustic soda solution. The first method is expensive and is used only in the treatment of valuable oils when loss of oil is significant. Sulfonic acids and their sodium salts can be removed by treatment with such agents as alcohol, glycerol, etc., which are described in the chapter on Solvents. However, some of the sulfonic acids recovered from "white oils" are valuable by-products, and such oils may be extracted with alcohol solutions after the sulfuric acid treatment and then neutralized with alkalis. These operations serve to reduce the formation of emulsions and to recover the soaps. Such procedures are particularly applicable to oils treated with relatively large quantities of fuming acid, or oleum. However, before a procedure of this type is adopted, it must be carefully investigated in the laboratory, for all the sulfonic acid soaps are not necessarily valuable. These sulfonic acids, and patents pertaining to their preparation, are noted in Chapter III, page 126.

The addition of very small amounts of demulsifying agents to prevent the emulsification of the alkali solution with the oil, such as liquid rosin,⁴⁰ petroleum carboxylic acids,⁴⁵ oleic or naphthenic acids, alcohol, etc.,⁵⁸ involves additional expense. Moreover these substances may be harmful to the properties of the finished oil.

It is generally possible to avoid formation of these emulsions by taking one or all of the following precautions during the treatment: the oil, if not too viscous, should usually be washed with a medium-strong alkali solution, practically without agitation; the quantity of caustic used should be only a little in excess of that actually necessary for neutralization; and the temperature of the oil should be as high as possible to reduce the viscosity and yet not injure the color. Usually the caustic solution is applied to lubricating oils while they are still relatively cold, and then heating is begun. Sometimes the mixture is heated rapidly by circulating it through powerful heat exchangers.

Other methods for avoiding emulsions have been discussed, such as adding a small volume of fairly strong caustic soda solution and then adsorbing the resulting soaps with fuller's earth or similar adsorbents; treating the oils at high temperatures, under pressure; etc.⁵⁰

Emulsions can generally be resolved by the addition of fuller's earth or similar adsorbents and then filtering.¹⁴ It is reported⁷³ that emulsions formed by the naphthenic soaps produced in neutralizing lubricating oils can be broken by heating the oil for about two hours under pressure and agitating it with steam, the temperature being sufficiently high to give a water-vapor pressure of 60 to 75 pounds per square inch. Moreover, it is claimed that if the alkali is applied to the acid oil under these conditions, emulsification will not occur. One of the usual methods used by refineries for the resolution of petroleum emulsions, if such are unexpectedly formed, is to store the emulsified batch and then to dispose of it gradually by adding small portions of it to oils that are to be neutralized. This method is effective because the balance between the oil and alkali phases and the emulsifying agent is thereby disturbed, and the emulsion breaks. The method is slow, but it is less harmful to the quality of the oil than most of the accelerated methods that rely on demulsifying agents or acidification. Obviously it is possible to break the emulsions by acidifying them with small quantities of sulfuric acid, a method sometimes used in practice. Sometimes very slow agitation or gentle air blowing will break an emulsion by coalescing the fine droplets into larger ones. There is usually some reversion in color in an oil recovered from an emulsion because of the unavoidable extra handling.

It is usually not difficult to separate the alkaline solution from the oil. The greatest loss of oil in emulsions is not in the alkali neutralization but in the subsequent washing with water to remove the sodium soaps. Oils known to emulsify seriously, such as those treated heavily with acid, are best washed free of their soaps by first giving them the so-called "spray-wash." The oil is treated hot to improve settling. The water is added in fine streams without agitation; as the individual droplets are large, they settle quickly. The spray is continued until a large portion of the soap is washed from the oil; obviously a large amount of water is needed as no equilibrium concentration between the solution of soaps in the oil and in the water is established. However, formation of emulsions is thus avoided. After the oil is washed in this manner, the remaining soaps are washed from the oil in the usual manner. It is the experience of the authors that practically every oil can be freed of alkalies by this method.

Because of the present process of acidizing oil wells, the crude oil may contain so much inorganic salt—as much as one pound per barrel in extreme cases—that it must be removed before the oil can be distilled. Unless removed, the salts, espe-

cially calcium and magnesium chlorides, are hydrolyzed; and the resulting hydrochloric acid corrodes the distillation equipment. The salt is also deposited in the still.

Several methods have been devised for desalting crude oils.⁴⁴ They are in many respects similar to the methods used for breaking oil-field emulsions. They include heating the oil under pressure, treatment with chemicals, electric dehydration methods, and much less frequently, filtration or centrifuging. The choice of method depends on the type of oil and is determined experimentally.

The simplest method consists in heating the crude oil under pressure to avoid the loss of the low-boiling constituents and allowing the salts to settle. Best results are usually obtained if some water is added to the crude oil, and the mixture slowly agitated before settling. The quantity of water added and the degree of agitation are very important as excess agitation may actually lead to formation of stable emulsions which are difficult to resolve.⁴⁵ The above treatment may be combined with the chemical treatment by adding to the oil a demulsifying agent of the type used for dehydrating oil-field emulsions, such as sodium sulfite⁴⁶ or different types of Tret-o-lite. The separation is accelerated by the electrical (Cottrell) method.⁴⁶ Centrifuging or filtering may be used, but these methods are often more expensive than the foregoing, although the cost is reduced if the mixture is first passed through towers or columns packed with excelsior⁴⁷ or similar material.

In general, the desalting operations involve washing the salt from the oil under conditions that permit rapid separation of the water solution from the oil.

Difficulties encountered in washing the alkalis from the oil with water have led to the broad application of adsorbents to remove the sulfuric acid and acid sludge in the "dry neutralization" methods described in the chapter on Adsorbents. Although the emulsification occurring in the water-washing of alkali-treated oils is due mainly to the sodium naphthenate and sodium sulfonate soaps, certain lubricating oils, such as those of California, emulsify readily when such soaps are absent. The emulsions consist mainly of minute droplets of oil dispersed in water, *i.e.*, oil-in-water emulsions. The addition of small amounts of reagents, such as lime soaps, which tend to reverse the type of emulsion (to make the oil the continuous phase) and thus counteract the effect of the sodium soap, lessens emulsion losses. The lime soaps, however, remain dissolved in the oils and may impair their quality.

Calcium soaps form water-in-oil emulsions; and, as a general rule, sodium soaps form oil-in-water emulsions. However, this observation is true only for sodium soaps of low molecular weight acids; the sodium soaps of high molecular weight acids are conducive to the formation of water-in-oil emulsions like those of the calcium soaps. Little has been published on the resolution of emulsions of the oil-in-water type encountered by the refiners, but much has been published on the water-in-oil type which occurs in crude oils.⁴¹ Obviously if the two types of emulsions are brought together, they will tend to neutralize each other and break. Unfortunately, however, it is not practical to permit an emulsion of a refined oil to become contaminated with an unrefined oil.

Recovery and Utilization of Spent Alkaline Solutions

Partially spent sodium hydroxide solutions may be used for neutralizing strong acids in oils, although this practice is not in general use since naphthenic acids and phenols may be released from the spent alkali and redissolved in the oil.

It is common practice in some refineries to mix equivalent portions of alkaline and acid sludges for their mutual neutralization and to recover the separated oil. In some instances, the alkaline liquor is evaporated directly to a pasty consistency, calcined, and leached; the hot liquor, containing carbonates, is causticized with lime to produce caustic soda.⁵⁴ This method is not profitable in most refineries, although in isolated cases it may be economical, such as in the Baku district.¹²⁸

In one process carbon dioxide is introduced into the alkaline sludge, carbon dioxide from flue gases being suitable. After separation of the oily layer, the alkali is causticized with lime.²⁶ The point at which the introduction of the carbon dioxide should be discontinued is determined by adding barium chloride to the solution and testing the solution with phenolphthalein.⁸

In certain instances, the caustic soda used in extracting hydrogen sulfide and mercaptans is regenerated for re-use by boiling or steaming.^{1, 9}

Naphthenic acids are separated from spent alkali by salting them out as sodium soaps with strong sodium chloride solution. These soaps can be acidified with sulfuric acid and the freed naphthenic acids distilled with direct steam, though this distillation is somewhat difficult to carry out on a commercial scale because of the entrainment of crude products; for many uses the purification of the naphthenic acids is not necessary.⁵⁷ A patent specifies treating the oil containing organic acids with alkalies and then distilling the oil from the soaps while still in a strongly alkaline condition.³² The spent alkali solutions from kerosene treatment can be evaporated until the soap content is about 40 per cent, and then the soap can be salted out.¹¹⁰ The spent alkaline liquor can be freed of oil by treating with dilute methanol, warming, and settling; the upper layer contains the oils.⁸⁹

The naphthenic acids can be separated from the soaps by neutralizing them with sulfur dioxide, which Gurwitsch prefers to sulfuric acid, as the resulting sodium sulfite can be causticized with lime to yield calcium sulfite, a more valuable product than calcium sulfate. The free petroleum oil can be separated from soaps by heating with water under pressure. Similar treatment can be used for the alkaline sludges from acid-treated lubricating oils.³

TREATMENT WITH POTASSIUM HYDROXIDE

Potassium hydroxide is as a rule much more soluble in solvents than sodium hydroxide; but in its chemical activity in industrial processes, it usually functions as an equivalent of sodium hydroxide. Potassium hydroxide is much more expensive than sodium hydroxide, and its use is limited, especially in aqueous solutions. It is recognized, however, that potassium hydroxide is not always a simple equivalent of caustic soda.¹⁰¹ It can, for example, be used in the removal of elemental sulfur from oils when applied either in a finely divided state¹²⁷ or in solution in a non-aqueous solvent, such as alcohol. This method of removing sulfur is described further below under Treatment with Alcoholates. Sodium hydroxide is not nearly so reactive with elemental sulfur as potassium hydroxide. Vesselovsky and Kalichevsky¹²¹ find that an alcoholic solution of potassium hydroxide readily removes elemental sulfur from light oils, and an alcoholic solution of sodium hydroxide is almost inert. Kalichevsky⁶⁷ states that gasolines or other petroleum distillates containing both elemental sulfur and mercaptans may be treated under certain conditions to an advantage with a mixture of sodium and potassium hydroxides.

Potassium hydroxide is nearly three times as soluble in anhydrous ethyl alcohol as sodium hydroxide, and the strong alcoholic potash solution (or, at times, sodium hydroxide solution) can be used to effect thorough contact between the alkali and an oil. The quantity of alcohol used need not be large. Anhydrous ethyl alcohol is soluble in all proportions in light petroleum distillates. When an alcohol solution of an alkali is added to a petroleum distillate, the alkali is precipitated from the alcohol in the oil in an extremely finely divided state, perhaps molecular, since for an instant the mixture appears perfectly clear. In a second or two the molecules of the alkali coalesce sufficiently to produce a visible white cloud in the distillate. The alkali in the fine state of division is ideal for thorough contact with the reactive constituents of the oil and, being free from water, can bring about reactions impossible in aqueous solutions. For some purposes methyl alcohol is preferable to ethyl alcohol because of its greater ease of recovery from the oil. It is less soluble than ethyl alcohol in the oil.

Investigations have shown that when a fraction of a per cent of potassium hydroxide in alcoholic solution is added to a fairly well-refined lubricating oil and the whole commingled with a pulverized adsorbent earth at 200 to 300° F. and filtered, the acid number of the oil can be reduced to a low figure.⁹⁸ Different earths function differently in this respect; Florida fuller's earth adsorbs the soap quite efficiently. The use of potassium hydroxide for the removal of organic acids from lubricating oils

without the aid of adsorbents is patented.²⁸ If such treatment is applied, it is suggested that the inorganic and strong organic acids be removed from acid-treated oils with sodium hydroxide, and the weaker organic acids with a potassium hydroxide solution at 250 to 285° F.

TREATMENT WITH SODIUM CARBONATE

Sodium carbonate is sometimes used as a substitute for sodium hydroxide for neutralizing inorganic acids in light oils because of its lower cost.⁴ It is usually less satisfactory than sodium hydroxide, as it does not remove the weakly acid constituents so completely, and the liberated carbon dioxide gas tends to emulsify a heavy oil. To obviate the first difficulty a procedure has been patented⁹¹ for treating first with a limited amount of solid sodium carbonate and then with sodium hydroxide or adsorbents. However, some American refiners claim that sodium carbonate gives as satisfactory results as sodium hydroxide.¹¹ The sodium carbonate is applied to the oil in the form of an aqueous solution⁵ or a dry salt. In order to minimize emulsification, a process has been patented for the addition of sodium chloride to the sodium carbonate.²

The preferred strength of the aqueous soda ash solution is from 10 to 20 per cent. The residual acidity of the oil is higher when the treatment is carried out in the cold because of the retention in solution of a greater amount of carbon dioxide.⁵⁶ Distillation of an oil in contact with sodium carbonate has also been recommended.¹²⁰

TREATMENT WITH AMMONIA

Ammonia is used in many refineries to neutralize the acid constituents of the oils and to protect equipment from the corrosive products of the oil. With the greater production of ammonia in the United States and consequent lower cost, its use in refineries will doubtless increase. If purchase prices are compared on combining weights, anhydrous ammonia is now a little cheaper than caustic soda.

The mechanical handling of ammonia in a refinery is simplified because it is volatile and maintains a steady flow, and because its solubility and high rate of diffusion lead to rapid neutralization of the acidic constituents of the oil. The solubility of the ammonia in oil increases with pressure.

Ammonia is used in cracking operations to prevent corrosion.²⁰ It is also used in condensers, fractioning towers, etc., although aqueous solutions of soda ash, caustic soda, or even aqueous suspensions of lime (milk of lime) have thus far been more popular for this purpose.

Anhydrous ammonia is used at times to advantage for the neutralization of the residual "acid" in lubricating oils; it destroys the acidity with-

out the formation of aqueous alkaline emulsions.⁴⁷ The excess ammonia can be blown out with air or inert gas. The ammonium sulfate produced in the neutralization can be settled from the oil on heating or by contacting the oil with adsorbents. This procedure of neutralizing the residual acid is primarily suitable for use on very viscous oils and in laboratory investigations. Almost all the acid sludge should be separated from the oil before the ammonia is added, as otherwise ammonium sulfate remains in the oil and is detrimental to the finished oil. The process can be continuous.¹⁴ Maitland⁷⁸ has observed that a small amount of ammonia added to an acid-treated oil after the main bulk of the sludge is removed accelerates the settling of the acid sludge. The oil can then be completely neutralized with sodium hydroxide. Ammonia can be used in an alcoholic solution, as shown by Fairweather,⁴⁶ who neutralizes acid-treated liquid petrolatum with a solution containing one volume of strong ammonium hydroxide to two volumes of alcohol.

The desulfurizing action of ammonia is the subject of several patents which cover treatment both in the liquid and in the vapor phase.⁷⁷ According to these patents, ammonia is dissolved in the oil under pressure, and the mixture forced at a high velocity through tubes heated to 400 to 550° F. or, if cracking is desired, to 550 to 700° F. Some of the sulfur is converted into sulfides or similar compounds easily removed by dilute sodium hydroxide solution. The oil can be treated in a similar manner in the vapor phase. It appears certain, however, that such treatment does nothing more than neutralize the hydrogen sulfide and the other corrosive products. A slightly different claim is made by Lucas⁷⁶ in later patents for simultaneous hydrogenation and desulfurization during cracking. In this process ammonia or a mixture of ammonia and hydrogen is supplied to the oil as it enters the cracking retort, which may contain a catalyst.

TREATMENT WITH LIME

Lime, because its initial cost is only about a seventh that of sodium hydroxide, can at times be used as a substitute for sodium hydroxide, and has been investigated for use in neutralizing certain oils.¹¹⁹ It has been used to treat natural, straight-run, and cracked gasoline. It can be added to crude oil in straight-run or in cracking stills to lessen or prevent the corrosion from hydrogen sulfide and other corrosive compounds. In the cracking units it is used also to change the character of the coke and sediments so as to prevent their settling from the oil in the stills. Its use, however, for the treatment of distillates is not always entirely satisfactory, as the calcium salts of the naphthenic or other organic acids are slightly soluble in oil, the time of agitation to effect neutralization is usually longer

than with sodium hydroxide, and the alkaline sludge settles slowly and is difficult to remove from the agitators because it is insoluble in water.

The lime soaps are inclined to retain a large quantity of emulsified oil,⁵⁸ and emulsions of the water-in-oil type are formed because of the solubility of the lime soaps in the oil. Sodium hydroxide, as stated above, usually forms the reverse type of emulsion; for this reason, a mixture of lime and sodium hydroxide may occasionally reduce the emulsification. However, the ash content of the neutralized oil is usually higher even with the mixed treatment than with caustic soda alone. It is claimed, however, that the organic acidity, as well as the inorganic acidity, may be removed when oil neutralized with lime is finally filtered through adsorbents.¹⁰⁸ Nevertheless, if powdered lime or milk of lime is used for neutralizing naphthenic acids in lubricating oil, the oil when finally freed of the soap does not readily emulsify, but may have a darker color, high cold test, and naphthenic acid odor, even after treatment with bleaching earth.⁷⁵

When lime as a 2 per cent suspension in water is substituted for sodium hydroxide, the refined oil is said to have a slightly darker color and higher ash content.¹⁰⁹ According to Redwood,¹⁰⁰ slaked lime is used for neutralizing distillates in some of the smaller Caucasian refineries. The oil is treated with about 3 to 5 per cent of lime, allowed to settle for two to three days, and then treated with about 0.05 per cent of sodium hydroxide. The loss of oil from emulsions because of the lime is said to be twice as large as in straight caustic treatment.

The quality of the lime to be used in a refinery should be evaluated by conventional tests, such as those described by Armsby.¹⁰

If lime is used in neutralizing acid-treated kerosene, a little organic lime salt may remain dissolved in the oil. When the oil is burned in a lamp, the lime collects in the wick and soon causes smoking and the other annoyances characteristic of an inferior grade of kerosene.

Kendall⁶⁹ finds that by adding finely divided quicklime to a large volume of cold water, about one pound of the lime to one barrel of water, the resulting finely divided hydrated lime remains in suspension in the water. The suspension is used to neutralize acid-treated naphthas, such as cracked gasolines.

Removal of acidic substances by a suspension containing 2 to 3 per cent of calcium and ferric hydroxides under pressure and in absence of air has been patented,³⁵ primarily for the removal of hydrogen sulfide from gasolines.

The use of calcium carbide instead of lime for neutralizing acid-treated oils has been recommended.¹²²

Both quick and hydrated lime at elevated temperatures have been investigated for removing sulfur, but have not been satisfactory. However, distilling the oil in contact with lime¹¹⁶ has some value for removing the organic acids from the distillate.

Various patents refer to heating petroleum with lime: the oil and lime are heated in open vessels;³³ dehydrated oil is heated with calcium oxide;³³ raw oil is treated with one per cent of quicklime under 50 atmospheres' pressure and at 570° F. for 30 minutes to reduce the sulfur content;³³ oil vapors are condensed in contact with water solutions of lime, litharge, lead acetate, or caustic soda,⁴⁰ etc. The use of filters containing animal black for filtering the oil after vapor phase refining with calcium and magnesium oxides is patented.¹²

Treatment of gasoline in the vapor phase with lime has been considered, but appears never to have been used.¹²

In some patents lime is recommended as a catalyst for the cracking of oil,¹⁰³ or for use in crude oil stills in which the residuum is distilled and reduced to asphalt. The asphalt produced is said to be homogeneous and acid-free; the distillate from the residuum is almost neutral, as the naphthenic acids are retained in the still; the color of the distilled oil is improved; and the distillate needs only a relatively small quantity of sulfuric acid for further refining.⁹⁰ However, it seems doubtful whether asphalt containing lime soaps is satisfactory for most purposes.

TREATMENT WITH MAGNESIUM HYDROXIDE

Magnesium hydroxide has been considered as an inexpensive neutralizing agent and for some purposes as a substitute for sodium hydroxide, but objections similar to those mentioned in connection with lime have prevented its extensive use in petroleum refining. Magnesium oxide has been patented for use in manufacturing a solid petroleum fuel, one part of magnesium oxide being mixed with as much as four parts of oil.¹⁶

The naturally occurring magnesium hydroxide (brucite) has met with favor for neutralizing the sulfuric acid of light acid oils. The acid oil is percolated through towers of granular magnesium hydroxide. The resulting magnesium sulfate is soluble in water and separates from the oil or can be washed from it, provided there are no organic acids present to yield magnesium soaps, which are slightly oil-soluble and cannot be removed by water washing. The granular magnesium is kept moistened with water to make it chemically reactive with the acid. When the tower becomes sluggish because of the accumulation of the magnesium sulfate, it is revived by a wash with water, which again exposes the fresh surfaces of the crystals. If brucite is used for sweetening purposes, sufficient sulfur is added to the gasoline before it is passed through the tower to convert the mercaptans to disulfides, according to the general reactions described in the chapter on Sweetening; difficulties are encountered, however, in sweetening certain types of cracked distillates. When the brucite becomes inactive, after approximately 1250 barrels of gasoline is used per ton of brucite, it is regenerated by a wash with a weak solution of sodium hydroxide at boiling temperature, followed by a wash with hot water

and drying. It is claimed that brucite can be successfully used for removing phenols and other acidic bodies from the distillates and for desulfurizing gases containing hydrogen sulfide.⁵¹

It is well known that calcium and magnesium soaps are very detrimental to the burning qualities of kerosene.⁵⁸ It is, however, of interest that 0.1 per cent of either in lubricating oils will stabilize the color of the oil in storage. The oleate may be a little more effective than the naphthenate of these elements.

TREATMENT WITH SODIUM SILICATE

The water-soluble alkali silicates have been used in many industrial processes in which a milder alkali serves better than the strong caustic alkalies. The silicates have been investigated extensively for use in purifying petroleum products because of their alkalinity and their tendency to coagulate and to adsorb colored and other objectionable constituents. Some favorable results have been obtained, but only a few of the many references are submitted here.

One of the early reports on the use of silicates states that the alkali silicates can be used alone or in solution with stronger alkalies in neutralizing light oils after the acid treatment. The precipitated silica or silicic acid assists in the decolorization of the oil.¹³⁰ Besides the bleaching, a certain desulfurizing action also is claimed to occur,⁵³ although it is obvious that only the sulfur in distinctly acidic molecules would be affected. For treating special fuel oils, a process is described in which the oil is treated with 5 per cent by weight of concentrated sulfuric acid; the acid-treated oil is then neutralized while hot with a strong solution of sodium silicate, settled, and filtered through silica gel.¹¹⁸

TREATMENT WITH CALCIUM CARBONATE

Calcium carbonate obviously has a limited use in a refinery. It has been recommended for neutralizing acid oils, but this use is objectionable for the reasons explained in the discussion on Treatment with Lime and Magnesium Hydroxide.

TREATMENT WITH SOAPS

The general literature on the use of soaps in treating petroleum products is discussed briefly in the following pages. As a rule, it can be said that the results obtained in refining with soaps can be secured much more economically by other methods and with less serious contamination. Experience has shown that soaps are economical in the oil industry only in the manufacture of greases and emulsions, and in some instances in serving to change one type of emulsion into another; in addition, however, the use

of soaps as inhibitors is rather widespread. Such uses are discussed elsewhere in this volume.

In one patent, soaps are used to coagulate impurities in spent lubricating oils.⁸² In another patent, crude oil and its fractions from topping operations are claimed to be improved by treatment successively with a soap solution, with sulfuric acid, and with alkali;⁸⁴ the soap is designed to reduce the quantity of acid needed and to lessen the emulsification during treatment.

Petroleum distillates may be desulfurized to a slight degree by passing their vapors through a solution of metal soaps. Frasch uses metallic oleates and colophonates.³⁷

The treatment of cracked distillates in the vapor phase with "Seafoam," manufactured by the Palmolive-Peet Company, has been patented for improving color. In this treatment the cracked oil is first distilled with steam to reduce the quantity of acid needed for treatment. The acid-treated distillate is then redistilled with the aid of steam and treated in the vapor phase with "Seafoam."⁵²

According to one patent, wax is separated more easily from oil when the oil is first treated with a soap solution;⁷⁰ the concentration of the soap solution is sufficiently low, however, to avoid emulsification. If wax is washed with soap solution before "sweating," the colloidal solids are said to be removed, and the crystals of the wax thereby obtained are larger and more uniform.³⁸

Processes have been patented for the conversion of liquid petroleum into semi-solid products by means of soaps. For example, a solution of soda soap, charged with several times its weight of sodium silicate, is added to the oil; the whole mixture is then heated to about 105° F. and allowed to cool and solidify.⁶⁹ The oil may also be solidified by means of an aqueous soap solution if sodium chloride is added in such definite quantity that a very small further addition would begin to "salt out," or precipitate, the soap.¹¹³ The sodium chloride is claimed to be beneficial in decreasing the soap consumption and rendering the process more economical.

Mineral oils are made emulsifiable with water when heated with a paste consisting of a mixture of solid sodium soaps made from sulfonated vegetable oils.⁶³ Mineral oils are made miscible with water by adding rosin oil and a solution of an alkali.¹⁷ Soaps are also effective in producing emulsion products from asphalts and other similar heavy oil products.¹²³ Soaps, such as calcium or magnesium oleate, can be used to stabilize particles of coke suspended in cracked residuum.⁸⁵

For other pertinent data on the manufacture of solid products and greases from petroleum oils, the reader is referred to the treatise of Klemgard⁷² and other literature on the general subject of greases.

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Chapter V

Sweetening Operations, Elimination of Elemental Sulfur, and Reduction of Total Sulfur in Light Distillates

The presence of elemental and combined sulfur in petroleum introduces special problems in the refining of the lower-boiling fractions, such as the gasolines and kerosene. The sulfur in the higher-boiling petroleum fractions, except for traces of hydrogen sulfide, is generally in the form of stable and neutral organic compounds, which have no deleterious effect on the oil; generally no effort is made to remove them.

The sulfur compounds occurring in petroleum may be classified as in Table 31.

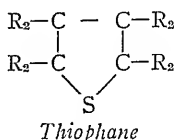
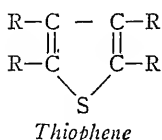
Table 31. Sulfur and Sulfur Compounds in Petroleum.

Elemental sulfur	S
Hydrogen sulfide	H ₂ S
Mercaptans	RSH
Disulfides	R ₂ S ₂
Sulfides	R ₂ S
Thiophenes	C ₄ H ₄ S

The low-boiling petroleum fractions, like gasoline, occasionally contain elemental sulfur in small proportions, which must be removed by special procedures. Hydrogen sulfide is nearly always present and is removed by any simple method of washing the hydrocarbons with an aqueous alkaline reagent, such as caustic soda, soda ash, lime, etc.

Cracked naphthas nearly always contain small quantities of mercaptans, which have an objectionable odor and other undesirable properties. The mercaptans are reactive chemically; they are acidic and are easily oxidized. Sometimes they are extracted from the oil quantitatively, but usually a portion of them is removed by caustic soda solution; the remainder is commonly transformed by a special oxidation procedure, "sweetening," into the less odoriferous alkyl disulfides, which remain dissolved in the oil.

In addition to the above sulfur compounds, there is in all petroleum products a much greater percentage of combined sulfur in a highly stable form; these compounds usually have thiophenic or thiophanic grouping, in which the sulfur atom is divalent, the two valences being attached to two different atoms of carbon, thus:



The R groups represent hydrogen atoms or hydrocarbon radicals. In the usual routine sulfur analyses of light petroleum distillates, this stable sulfur is commonly referred to as the residual sulfur.

Because of the chemical inertness of these sulfur compounds their removal from oil is usually very difficult. Up to the present they have been removed least expensively by means of strong sulfuric acid at low temperatures and by liquid sulfur dioxide, as described in Chapters II and VII.

In this chapter are discussed first the subject of sweetening, involving elemental sulfur and mercaptans, and secondly, the general subject of the reduction in the total sulfur content in light petroleum products.

Laboratory Analysis of Oils for Various Sulfur Compounds

Several processes have been suggested for the identification of different types of sulfur compounds occurring in gasoline and other light petroleum distillates. Hydrogen sulfide reacts with soluble lead salts to form black lead sulfide, or with cadmium salts to form yellow cadmium sulfide, and is easily washed from the oil with alkali solutions; elemental sulfur forms mercury sulfide on agitating the oil with mercury; and disulfides can be reduced to mercaptans and then identified by treatment with sodium plumbite and sulfur. Certain low molecular weight sulfides can be precipitated from the residual oil with mercuric chloride or acetate,³⁹ and the residual organic sulfur determined by the lamp method.⁹⁷

A distillate containing mercaptans (or hydrogen sulfide) is said to be "sour," or to be positive, in the common "doctor test"; and if it does not contain the mercaptans (or hydrogen sulfide), it is "sweet," or negative, in the doctor test. In this doctor test, sodium plumbite reacts with mercaptans, forming a yellowish, insoluble lead mercaptide, which darkens quickly when elemental sulfur is added, usually through color stages of orange to brown.

The method of making the doctor test in the laboratory has been investigated by the Atlantic Refining Company.^{70, 242} They find that the volume of the sample and the interfacial area are important for duplicating tests. According to their procedure, 10 cc. of the sample of oil to be tested is added to 5 cc. of sodium plumbite solution (120 to 140 grams sodium hydroxide and 20 to 30 grams litharge per liter) in a standard test bottle (4-ounce sample bottle, 33 mm. inside diameter, fitted with a clean cork stopper). The bottle is stoppered, shaken for 15 seconds, and dry flowers of sulfur (ground and screened to 100 to 200 mesh) added to the mixture in quantity just sufficient to cover the interface (20 to 25 mg.). The bottle is again stoppered and

shaken for 15 seconds. The test is reported positive if either the oil or the sulfur becomes discolored.

The sensitiveness of this test for different mercaptans has recently been examined by Henderson, Agruss, and Ayers.¹⁸² The data for the minimum amount of mercaptan sulfur required to give a positive doctor test in a sample of Stoddard cleaners' solvent is shown in Table 32.

Table 32. Sensitivity of the Doctor Test* with Solutions of Mercaptans in Naphtha.

Mercaptan	Minimum % by Weight of Mercaptan Sulfur in Naphtha Required to Give Positive Doctor Test
Ethyl	0.0006
<i>n</i> -Propyl	0.0003
<i>n</i> -Butyl	0.00015
<i>n</i> -Amyl	0.0002
Isoamyl	0.0001
<i>n</i> -Heptyl	0.0001
Phenyl	0.0010

* Federal Specifications VV-L-791a.

Mercaptans are commonly determined quantitatively by one of the three following methods:

Silver nitrate and ammonium thiocyanate method.⁴⁰ The mercaptans are precipitated with an excess of standard silver nitrate solution, and the excess silver nitrate titrated with standard ammonium thiocyanate. A modification to simplify the method by the addition of alcohol has been made by Malisoff and Marks¹⁶⁷ and by Malisoff and Anding.¹⁶⁶ The method is accurate and direct, but is difficult in highly colored naphthas.

Potentiometric method.²³⁵ The mercaptans in the naphtha are titrated directly in a solution of isopropyl alcohol and sodium acetate with standard silver nitrate solution, and the end point determined potentiometrically. An excess of silver nitrate is obviated; and as the end point is not dependent upon a color change of an indicator, colored as well as colorless solutions can be titrated.

Direct titrations with copper sulfate in ammonium hydroxide solution.¹⁹ The solution is prepared by (a) dissolving 3.928 grams of pure hydrated copper sulfate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, in 300-400 cc. of water; (b) chilling with ice chips; (c) slowly adding about 25 cc. of cold 5 per cent caustic soda to precipitate all the copper as $\text{Cu}(\text{OH})_2$; (d) adding a few hundred cc. of ice-cold concentrated ammonium hydroxide to dissolve all the copper hydroxide; and (e) diluting the solution to exactly one liter. The final solution is stable. One cc. of the solution is added at a time to the sample of sour gasoline, which is agitated until the blue color disappears. This procedure is continued until a slight excess of the copper has been added, as indicated by the permanent blue color. Each cc. of the copper solution is equivalent to one mg. of mercaptan sulfur. The hydrogen sulfide is first

removed from the sour naphtha sample by washing with a little dilute soda ash solution.

In an older method of analysis, developed by Wendt and Diggs,²⁵⁵ the hydrogen sulfide is first removed by means of acid lead acetate, and the gasoline then divided into two portions. One portion is treated with a small amount of one per cent ethyl mercaptan solution and sodium plumbite. The excess of lead mercaptide is removed with dilute acetic acid, and the amount of lead sulfide left is a measure of the elemental sulfur originally in the oil. The mercaptans are determined in the second portion of the solution by a similar procedure, with the exception that elemental sulfur instead of mercaptans is added in excess to the oil, and the lead sulfide formed is a measure of the mercaptans present.

Wertheim²⁵⁶ gives methods for the identification of the different mercaptans. Borgstrom and co-workers³⁷ investigated the effect of various agents on naphtha solutions of mercaptans under different conditions of treatment (copper and mercury salts, acetates of metals, oxidizing agents, sodium hydroxide, sodium plumbite, etc.).

Corrosiveness, and Tests for Corrosiveness in Oil

Over a dozen sulfur compounds occurring in crude oil, as well as elemental sulfur itself, are corrosive or conducive to corrosiveness. Among these compounds are mercaptans, hydrogen sulfide, alkyl sulfates, sulfonic acids, and alkyl disulfides. Other compounds, such as carbon disulfide, sulfoxides, sulfones, and thiophenes, are only slightly corrosive, if at all.^{215, 261} Heat and moisture increase the corrosiveness. Elemental sulfur, after the elimination of hydrogen sulfide, is usually considered the chief cause of corrosiveness, but other substances may be corrosive, especially if the corrosion tests are made at 212° F.²⁴²

Of the various metals, copper, silver, bismuth, and mercury are especially prone to corrode in the presence of active sulfur compounds; chromium and tin are less sensitive.^{170, 261} Though copper is now used officially in making corrosion tests, bismuth might be superior, especially in evaporating the oil in metallic dishes. The oil residue can be removed easily from bismuth by ether or benzene, and the corrosion of the metal detected by the characteristic gunmetal color.¹⁷⁰

It is of practical importance to know that there is no relationship whatever between the total sulfur content of oils and the degree of corrosiveness,⁹⁰ and that elemental sulfur (and for this reason possibly other substances also) is more corrosive in the presence of certain types of combined sulfur,¹⁵ even though the combined sulfur itself may not be corrosive.

The presence of corrosive substances is shown by the "corrosion test," included in the specification tests on motor fuels.²⁴² The usual official test for corrosiveness is made either by evaporating the light oil in a freshly polished copper dish* or by immersing a polished strip of copper in the

* This method does not differentiate sharply between the gums and actual sulfur corrosion.¹⁷⁰

oil at a certain temperature and for a definite length of time.²⁴² It is possible to accelerate the test by exposing copper to the action of the oil for a shorter time but at a higher temperature. Thus heating gasoline under reflux condensation for about ten minutes at 240° F. produced somewhat the same effect as the three-hour test at 122° F. or a 30-minute test at 200 to 212° F.^{55, 132} Such a method is not entirely satisfactory, as some substances not corrosive at low temperatures are decidedly corrosive at elevated temperatures. It has been recommended^{184, 210} that accelerated tests for corrosion be made by contacting the oil with mercury at room temperature, filtering the mercury, and then judging the degree of corrosiveness by noting the intensity of the black precipitate which is left on the paper. This method is too sensitive to check the copper strip or copper dish method, and it alone cannot be relied on as a test for elemental sulfur, since it has been shown by Antropoff¹⁰ that petroleum peroxides give a black deposit with mercury. However, under ordinary conditions the mercury generally can be used advantageously to indicate the excess of sulfur added in plumbite sweetening. The mercury is darkened quickly by elemental sulfur and slowly by polysulfide sulfur.

A quick and accurate determination of the corrosiveness of gasoline caused by elemental sulfur can be made by adding to the gasoline a solution of mercaptans and agitating the mixture with sodium plumbite solution. An immediate dark discoloration is due to elemental sulfur, provided the gasoline has already been freed from hydrogen sulfide by washing with soda ash solution or otherwise. This process is in practical use in many refineries for control in the sweetening operations. It is entirely reliable for oils which have been sweetened by the use of elemental sulfur and plumbite solution. It also indicates "potential" corrosiveness in a gasoline, such as straight-run gasoline, which has a fairly high content of elemental sulfur but is completely free from mercaptans and which has not been exposed to sunlight. If this gasoline is blended with other gasoline bearing a trace of mercaptans, *e.g.*, a cracked gasoline, it will then be corrosive to a copper strip. Mercaptans are not corrosive to copper, nor even to metallic mercury, unless elemental sulfur is also present, and the latter in quantities as great as 150 mg. per liter of gasoline is not corrosive to copper, even at 122° F. for three hours, unless mercaptans are present or unless the oil-sulfur solution is exposed for 5 to 40 minutes to the direct rays of the sun or to ultraviolet light. Under either of these last conditions, as little as 10 to 15 mg. per liter of sulfur (slightly over 0.001 per cent by weight) is corrosive to copper.²²⁹ Recently Happel and Cauley¹²⁷ have investigated the influence of various concentrations of mercaptans and elemental sulfur, when dissolved together in gasoline, on the A. S. T. M. copper strip corrosion test at 122° F. for three hours. Table 33 gives the significant data.

Table 33. Effect of Elemental and Mercaptan Sulfur in Gasolines upon A.S.T.M. Corrosion Test.

Blends % by Weight		Results of A.S.T.M. Corrosion Tests		
Mercaptan Sulfur	Elemental Sulfur	Gasoline A	Gasoline B	Gasoline C
0.001	0.001	OK	OK	OK
0.001	0.002	Slightly corrosive	OK	Slightly corrosive
0.001	0.003	Corrosive	Corrosive	Corrosive
0.002	0.001	OK	OK	OK
0.002	0.002	Corrosive	Corrosive	Corrosive
0.002	0.003	Corrosive	Corrosive	Corrosive
0.005	0.001	OK	OK	OK
0.005	0.002	Corrosive	Corrosive	Corrosive
0.005	0.003	Corrosive	Corrosive	Corrosive

Although any of the low molecular weight mercaptans can be used to make the test for elemental and polysulfide sulfur (usually designated as "active sulfur"), butyl mercaptan is widely used in most refineries in the following manner:¹⁰²

To 30 cc. of gasoline in a 4-ounce oil sample bottle is added 20 cc. of a dilute butyl mercaptan solution (1 to 1400 by volume in cleaners' naphtha, containing no elemental sulfur), followed by 10 cc. doctor solution. The bottle is shaken for 15 seconds. The sample should then be light yellow-green in color and transparent. An orange or brown color forming immediately (less than about 5 seconds) denotes elemental sulfur in such form as to make the gasoline corrosive. On the other hand, a slow darkening (a few minutes to an hour or more) of the color in this test of a gasoline sweetened with elemental sulfur and plumbite solution shows that even though the gasoline will pass the copper strip corrosion test, sufficient "active" sulfur is present (most probably as alkyl polysulfides) to lower the lead and inhibitor susceptibilities and the color stability.

Wirth and Strong²⁵⁸ determine the quantity of active sulfur in gasoline by adding a known quantity of butyl mercaptan (in excess) to the sample, agitating the mixture with plumbite solution to cause the sulfur to react, and then removing the doctor solution and determining the excess of mercaptan in the gasoline by the silver nitrate or other method.

Comay⁶¹ finds that peroxides, such as the petroleum peroxides, inhibit the corrosive action of elemental sulfur on copper in the copper strip test. For example, 100 mg. of sulfur in 100 cc. of an oxidized gasoline had not affected a copper strip after several hours at 212° F., but when the peroxide was destroyed by reduction, the sulfur in a few minutes produced heavy corrosion and scaling of the copper strip.

Comay shows that an accurate and practical method for the quantitative determination of elemental sulfur in gasoline is to convert the sulfur *in situ* to hydrogen sulfide generated from powdered iron and hydrochloric acid, expel the hydrogen sulfide from the gasoline, absorb it in ammoniacal cadmium chloride solution, and titrate the precipitated cadmium sulfide with iodine solution. The test can be completed in twenty minutes.

SWEETENING OPERATIONS

The treatment of the light petroleum oils, especially cracked gasoline, with the more usual refining agents, such as sulfuric acid, alkalis, adsorbents, etc., may still leave them unmarketable because of the mercaptans, or thioalcohols. In addition to the odor the mercaptans have other undesirable properties; if elemental sulfur is also present in the oil, even

in traces as low as 0.001 per cent, the two react with each other and make the oil corrosive to metals. Such solutions are also conducive to the discoloration of the gasoline. Inasmuch as the mercaptan sulfur generally constitutes only a small fraction of the total content of sulfur in light distillates, the refiners of mercaptan-bearing stocks have usually considered it economical to extract part of the mercaptans with aqueous caustic soda solution and then to convert the rest of the mercaptans into more innocuous compounds, which remain dissolved in the oil, rather than to remove them from the oil. However, as all sulfur compounds are now known to lower the lead susceptibility of gasolines, methods of sweetening are desired which will remove all the sulfur possible.

The oldest and best known process of treating stocks containing mercaptans subsequent to the caustic soda wash is the "doctor," or plumbite, treatment, which consists in agitating the mercaptan-bearing naphtha with a little sulfur and an aqueous alkaline solution of sodium plumbite. The mercaptans are converted to alkyl disulfides, and to some alkyl polysulfides if too much elemental sulfur is added.

Other sweetening processes, developed during the last few years, have displaced the plumbite process in many refineries. Among these processes are: the use of the lead sulfide as a catalyst to convert mercaptans to disulfides by the oxidizing influence of atmospheric oxygen; the use of cupric salts in aqueous solution to oxidize the mercaptans (the cupric salt is reduced to the cuprous salt but is reoxidized to the cupric condition by air); oxidation of the mercaptans by a hypochlorite solution; and the extraction of some or all of the mercaptans by aqueous caustic alkali solutions, the solvent power of which for the mercaptans is enhanced by a second substance (a solutizer), such as sodium isobutyrate.

The sweetening methods will be discussed in the following order:

- (1) Oxidizing mercaptans by elemental sulfur.
- (2) Oxidizing mercaptans by oxygen or air.
- (3) Oxidizing mercaptans by alkali hypochlorite.
- (4) Extraction of mercaptans.

Sodium Plumbite Treatment

For many years it has been the practice to treat certain petroleum distillates, like gasoline and kerosene, with a very definite amount of sulfur and an aqueous solution of sodium hydroxide and sodium plumbite, usually termed the "doctor solution," to eliminate the mercaptan odor and to render non-corrosive a distillate which contains both elemental sulfur and mercaptans. The doctor solution is also used to remove elemental sulfur by the addition of a definite quantity of mercaptans with the plumbite solution. The plumbite solution effects a chemical reaction between mercaptans and

elemental sulfur; the mercaptans are converted into dialkyl disulfides, and doubtless into some dialkyl polysulfides, and the sulfur mainly into sulfides, polysulfides, and thiosulfates of soda and of lead.

Hydrogen sulfide combines with sodium plumbite, or doctor solution, to form lead sulfide, but it is removed more economically from a distillate by washing with an aqueous alkali solution.

It is difficult to add the proper amount of elemental sulfur to the oil during the doctor treatment in a refinery. If too much is added, the excess remaining in the oil, unless reduced to about 10 parts per million, may render the gasoline corrosive.

Except for the removal of hydrogen sulfide, the total sulfur content of an oil is generally not reduced by the doctor treatment unless the sweetened product is redistilled;²⁵² and even then the reduction is likely to be small. If a slight reduction is observed after the doctor treatment and steam or vacuum distillation, the reduction is primarily due to the fact that the alkyl disulfides and probably polysulfides produced from the mercaptans have higher boiling points than the parent mercaptans, and some of them remain behind in the still. It occasionally happens that the oil has present both elemental sulfur and mercaptans, and when this oil is sweetened with plumbite solution, all the elemental sulfur, or its equivalent, is removed as lead sulfide. To some degree there is an adsorption of sulfur and sulfur compounds by the precipitated lead sulfide, since the ratio of the lead to sulfur in the precipitate is by no means constant.

Table 34. Boiling Points of Mercaptans and Corresponding Disulfides.

Kind of Mercaptan or Disulfide	Boiling Point (° F.)	
	Mercaptan	Disulfide
Methyl	45	243
Ethyl	99	307
<i>n</i> -Propyl	155	379
Isopropyl	156	347
<i>n</i> -Butyl	208	(194 at 4 mm. pressure)
Isobutyl	190	419
<i>n</i> -Amyl	260	...
Isoamyl	243	482
<i>n</i> -Hexyl	305	...
<i>n</i> -Heptyl	349	(327 at 6 mm. pressure)
<i>n</i> -Octyl	390	...
<i>n</i> -Nonyl	429	...

Table 34 shows the boiling points of many of the mercaptans boiling below 430° F. and the known boiling points of the corresponding disulfides. The disulfides in this range boil from 191 to 239° F. higher than the corresponding mercaptans.

Table 35 shows the analysis of the sulfur in a typical gasoline before and after the doctor sweetening, but without subsequent distillation.¹²⁹

Table 35. Sulfur Analysis of Gasoline Before and After Sweetening.
(0.016% elemental sulfur was added for sweetening and is not shown in table.)

	Sulfur (% by Weight)	
	Sour Distillate	Sweetened Distillate
Elemental sulfur	0.000	0.010
Mercaptan sulfur	0.018	0.000
Residual sulfur ^a	0.151	0.170
Total sulfur	0.169	0.180

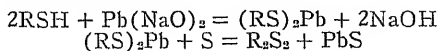
^a Residual sulfur here signifies sulfur other than elemental and mercaptan sulfur.

The Chemistry of Sodium Plumbite Treatment

Mercaptans are the principal, and nearly always the sole, constituents responsible for the positive doctor test and for the offensive odors of light distillates. Hydrogen sulfide reacts with the doctor solution and precipitates lead sulfide; but as lead is about ten times as expensive as caustic soda for removing hydrogen sulfide,⁵⁵ and as hydrogen sulfide is readily removed by caustic soda solution, it is customary first to wash the oil containing large quantities of hydrogen sulfide with caustic soda solution. Hydrogen sulfide can easily be distinguished from mercaptans, as it forms lead sulfide instantly with lead acetate or gives a black precipitate with sodium plumbite solution. Elemental sulfur alone, sulfonates, alkyl sulfides,* alkyl disulfides, sulfoxides, thiophenes, and carbon disulfide^{255, 260, 262} do not react with the plumbite solution.

Besides certain sulfur compounds, organic peroxides also give a positive doctor test, but they can be distinguished from the mercaptans by the addition of sulfur. If peroxides only are present, the sulfur does not intensify the color of the lead precipitate.^{46, 260} Color-forming compounds of the diolefin and terpene type are reported to react with the doctor solution.^{172, 210}

The reaction between the mercaptans, sodium plumbite solution, and sulfur proceeds about as follows:



These equations indicate that unless the elemental sulfur taking part in the reaction is already in the gasoline, the total sulfur content of the gasoline is not reduced by the doctor treatment. Moreover, they show that

* Alkyl sulfides do not react with the doctor solution, but when they are heated with sulfur, some reaction occurs, probably because of formation of a polysulfide, which eventually liberates hydrogen sulfide and gives a slight precipitate with sodium plumbite.²⁰⁰

elemental sulfur, as such, can be eliminated from gasoline by means of mercaptans and sodium plumbite solution.

Ott and Reid ¹⁸⁵ have investigated the reaction in treating mercaptans with sodium plumbite solution. They find that besides lead sulfide, compounds of the type $Pb_2S(SR)_2$, $Pb_2(OH)_2S_3$, $Pb_2(OH)_2S_4$, etc., are formed, and they assume that the reaction goes through the formation of unstable intermediate polysulfides, which decompose. They also find that the lead mercaptides behave like organic compounds and are soluble in the usual organic solvents. Atmospheric oxygen oxidizes them to fairly stable peroxides of high but varying oxygen content, such as $Pb(SR)_2O_8$, etc. (See also Billheimer and Reid ²¹ on the decomposition of mercaptans in alkaline solutions.) Borgstrom, Ellis, and Reid ²⁵ have described the preparation, properties, and reactions of lead mercaptides.

The foregoing equations do not always represent completely all the reactions involved in doctor treatment. According to the equations, lead sulfide only is precipitated, but in reality the precipitate may contain a comparatively small amount of lead sulfide.¹⁷³ Besides neutral mercaptides, basic mercaptides are also formed. The equation also indicates that one-half pound of elemental sulfur should be added per pound of sulfur present in the mercaptans. In practice, however, the quantity of sulfur added for complete reaction and subsidence, or settling, of the black precipitate is not so definite. The amount of sulfur over the minimum required to affect the oxidation can nearly always be increased by at least 10 to 20 per cent without making the gasoline corrosive to the copper strip in the exposure test for three hours at 122° F., although some of the extra sulfur above the minimum requirement remains in the gasoline in loose combination; almost certainly some is in the form of alkyl polysulfides with more than three atoms of sulfur per molecule. These polysulfides decrease the resistance of the gasoline to oxidation, as shown by the decreased induction period, and increase the gum content. They also lower the lead susceptibility ^{27, 218, 220, 241} and the inhibitor susceptibility.

The presence of the polysulfides in sweetened gasoline is usually easily detected, and they are easily differentiated from elemental sulfur by means of the color reactions in the test for corrosion with doctor solution and mercaptan solution, as discussed above under the tests for corrosion. It is usually possible in plumbite sweetening to control the amount of sulfur added so that no darkening of the yellow lead mercaptide occurs for a half hour up to three hours. Under these conditions too little active sulfur is present to affect the sweetened gasoline adversely.

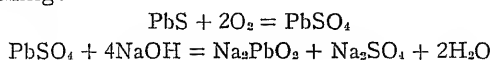
If not enough sulfur is added during the sweetening process, the oil usually turns brown from the formation of the intermediate reaction products, the lead mercaptides, and some lead sulfide, partly soluble or held in a colloidal state in the gasoline. These can be precipitated and the gasoline cleared by adding more elemental sulfur.

Through inability to secure good contact or other conditions, the reaction of the sodium plumbite solution with the mercaptans is rather slow. Low molecular weight mercaptans react more quickly than those of higher weight, but in either case considerable time is required for the reaction to go to completion.

The alkyl disulfides produced by the reaction of mercaptans with sodium plumbite and sulfur can be reduced to mercaptans by reducing agents. Nascent hydrogen converts them to mercaptans; but some of the very mild reducing agents, such as ferrous sulfate, are without effect on the sulfides and can be applied for other purposes to the gasoline, even after the doctor treatment, without causing the gasoline to become sour again.

The lower weight mercaptans can be extracted from light oils as lead mercaptides,²⁵⁵ but the higher weight mercaptans cannot, because the greater solubility of the larger hydrocarbon group of the mercaptan prevents such mercaptides from settling from the oil. Sulfur, therefore, must be added, which oxidizes the mercaptans to the disulfides and releases them from the lead.

Although experiments indicate that one atom of lead is capable of converting more than two molecules of mercaptans to alkyl disulfides, the mechanism of the process has been obscure. Morrell and Faragher¹⁷⁹ show that lead sulfide when exposed to air, especially at slightly elevated temperatures, is readily oxidized to lead sulfate. They find that lead sulfide, produced from the double decomposition of lead acetate and hydrogen sulfide and properly washed to free it from any lead sulfate, becomes oxidized to lead sulfate to the extent of 22 per cent during a normal drying operation in a drying oven. They also find that lead sulfide free from all oxidation products will not sweeten sour gasoline, even though the requisite amount of sulfur is present. By these observations they explain the phenomenon that a plumbite solution in which the total lead content has been converted into lead sulfide still displays power of sweetening if air is used in agitating it with sour gasoline, and if the necessary proportion of sulfur is available. They express as follows the preliminary changes through which the lead sulfide goes when agitated with air in the presence of caustic soda solution before it becomes active in the normal plumbite sweetening:



When this sodium plumbite is converted to lead sulfide in reacting with two molecules of mercaptans and one atom of sulfur, it is again converted by the oxygen and caustic soda to sodium plumbite. They also show that in sweetening with lead sulfide in the presence of caustic soda solution and

oxygen, the rate of sweetening is a function of the concentration and activity of the oxygen. Thus ozonized air requires one-third the time required by oxygen, and pure oxygen one-half the time required by air.

Happel and Robertson¹²⁹ determined in three experiments with doctor sweetening in which ample air was introduced that the consumption of litharge and sulfur was only 48 and 66 per cent, respectively, of the theoretical.

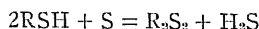
Lachman,¹⁵⁸ in an especially informational paper, reports some experiments on the rate of oxidation of mercaptans in gasoline by means of air and aqueous solution of caustic soda. In one hour 60 to 75 per cent of the mercaptans are oxidized to disulfides. The addition of small amounts of the sulfides of cadmium, zinc, and lead greatly accelerates the rate, although it appears to be much slower than when sulfur and plumbite solution are used for the oxidation. Likewise, powdered sulfur helps eliminate the mercaptans; and the data led Lachman to the conclusion that sulfur acts catalytically in accelerating oxygen; but doubtless the sulfur itself is the principal oxidant, inasmuch as sulfur in excess over the theoretical quantity required to react with the mercaptans completely sweetens sour gasoline in contact with an aqueous solution of alkali, the rate being much greater than oxidation by air under similar conditions. The process of using excess sulfur cannot be used commercially because of the corrosiveness of the excess sulfur. The sweetening effect with lead sulfide is, as to be expected, more rapid in the presence of both oxygen and sulfur. This oxidation by air and sulfur with lead sulfide has recently been investigated by Happel and Robertson and will be discussed later in the chapter.

Sweetened oils often become sour on redistillation. This change may be due not only to the decomposition of disulfides but also to the formation of hydrogen sulfide and mercaptans from elemental sulfur and olefins, as well as to decomposition products from the other sulfur compounds in the oil.

Faragher, Morrell, and Comay⁹⁶ have shown that ethyl and propyl disulfides can be distilled without decomposition, but the subsequent disulfides in the series having higher molecular weights decompose during distillation; butyl disulfide, for example, gives a trace of hydrogen sulfide and butyl mercaptan, and isoamyl disulfide gives a large quantity of hydrogen sulfide and about 9 per cent of the sulfur as isoamyl mercaptan. These investigators have also shown that mercaptans, when heated to 925° F. for a short time, are decomposed, a behavior which accounts for the absence of mercaptans in gasolines made in high-temperature cracking operations, such as in the vapor-phase processes.

High molecular weight mercaptans and sulfur may exist together in an

oil; but when heated to about 350° F., they react together, first forming disulfides and hydrogen sulfide, according to the equation:



The disulfide undergoes still further change.

A naphtha solution of sulfur after standing for six months may give a slight reaction with sodium plumbite solution, a change suggesting mercaptans, although alkyl peroxides are probably the cause of the positive test. It is the more common occurrence for a slightly sour gasoline to become sweet on standing.

Under the influence of light and heat, elemental sulfur in gasoline not only renders the gasoline corrosive but causes a reversion in color and a formation of gum.²⁵⁵ This effect on the color does not always occur.¹⁹³

As already shown, mercaptans are converted by the doctor treatment into disulfides, which are not removed from the oil, and certain of these are known to be in part responsible for the discoloration of gasolines in storage. Thus butyl disulfide, prepared by treating butyl mercaptan with doctor solution and also by treatment with sodium hypochlorite, was added in the amount of 2 per cent to a gasoline of 30 Saybolt color. In 24 hours the color of the gasoline reverted to 20 Saybolt and in two weeks to 10 Saybolt, the sample being kept in diffused light. A blank sample did not suffer any reversion in color.¹⁶ It is known that elemental sulfur and disulfides are often conducive to discoloration.^{134, 174}

It has been shown^{17, 91} that cracked gasolines sweetened with plumbite solution and sulfur may be considerably less stable in color when exposed to light (carbon-arc lamp) than the original sour gasoline, and that frequently the light produces a haze in the gasoline. The color instability is due to the disulfides and to a small amount of sulfur added in excess over the minimum necessary for sweetening. The removal of either helps the stability, but both must be removed to restore the original color stability of the gasoline to light.

As a rule, however, sweetening with the doctor solution when the amount of elemental sulfur is reduced to the minimum does not seriously affect the normal color or color stability of the product. In rare cases cracked gasoline may be discolored by the doctor treatment or even by caustic soda solution, but this discoloration can usually be prevented by a preliminary washing of the gasoline with water or by treatment with a reducing agent, such as ferrous sulfate. A long contact between the spent doctor solution and the oil is sure to injure the color of the oil. For this reason the gasoline which separates from the emulsified doctor solution on standing is not introduced into the finished product.

Lowry, Dryer, Wirth, and Sutherland have studied the effects on the gum content and resistance to oxidation of gasoline sweetened by the plumbite process in which a minimum amount of sulfur and amounts in excess of this minimum were added to the sour gasoline before sweetening. Table 36 is taken from their publication.^{162, 220}

Table 36. Effect of Sulfur in Sweetening West Texas Cracked Gasoline.

Excess sulfur (%)	0	0.005	0.0075	0.010	0.015
Induction period, min.:					
No inhibitor	200	210	115	125	100
0.013% U. O. P. inhibitor 4	380	400	285	210	175
Copper dish gum, mg./100 cc.:					
No inhibitor	299	273	327	389	357
0.013% U. O. P. inhibitor 4	5	6	74	82	138

The U. O. P. inhibitor 4 was used in greater percentage than in normal refinery practice, yet its effect was greatly decreased in the samples bearing a rather large excess of sulfur, although the sulfur was not sufficient in any case to make the gasoline corrosive to the copper strip.

Plumbite Sweetening and Octane Rating

Studies have been made on the influence of the sulfur compounds involved in doctor sweetening on the octane rating and especially on the lead susceptibility of the sweetened gasoline. Table 37 shows data developed by Birch and Stansfield²⁷ in adding 0.1 per cent organic sulfur to a sulfur-free gasoline of 64.4 octane value. The third column shows that, except for the trisulfide, these sulfur compounds do not greatly affect the octane values of the unleaded gasoline, but the last two columns show that the sulfur compounds make it necessary to add much more ethyl fluid than to the original sulfur-free gasoline to yield an octane number of 70.5. The disulfide sulfur is only slightly more detrimental than the mercaptan sulfur, but the trisulfide sulfur is much more detrimental.

Table 37. Adding 0.1% of Organic Sulfur to Sulfur-Free Gasoline: Effect on Octane Value and Tetraethyl Lead (TEL) Requirements.

Kind of Sulfur Compound Added	Actual Sulfur Added (%)	Octane No. after Addition of Indicated cc. of TEL		
		0	1	3
Gasoline alone	0.0	64.4	73.8	82.3
Gasoline + C_2H_5SH	0.1	63.6	68.7	74.3
Gasoline + $(C_2H_5)_2S$	0.1	64.6	70.5	76.6
Gasoline + $(C_2H_5)_2S_2$	0.1	64.0	68.8	73.4
Gasoline + $(C_2H_5)_2S_3$	0.1	62.0	66.6	73.0

Schulze and Buell²²⁰ also find that mercaptan sulfur and disulfide sulfur in gasoline have about the same effect in suppressing lead susceptibility. They show that the polysulfides are the most detrimental to the tetraethyl lead; then in decreasing order are the disulfides, mercaptans, sulfides, and thiophenes.

In Table 38 Birch and Stansfield show the influence of successively larger amounts of diethyl disulfide in decreasing the activity of ethyl fluid (3 cc. per gal.) on otherwise sulfur-free gasoline having an octane number of 65.

Table 38. Inhibiting Effect of Different Small Quantities of Ethyl Disulfide on Tetraethyl Lead in Sulfur-Free Gasoline of 65 Octane Number.

% Disulfide Sulfur in Otherwise Sulfur- free Gasoline	Octane No. with 3 cc. TEL per gal.	Octane Degrada- tion Due to Sulfur	Change in Degrada- tion per Incre- ment of 0.05 % Sulfur
0.00	84	0	0
0.05	78	6	6
0.10	76	8	2
0.20	73	11	1.5

It is observed in Table 38 that the first increment of disulfide sulfur in the otherwise sulfur-free gasoline is more active in suppressing the tetraethyl lead than the succeeding increments; the first 0.05 per cent depressed it by 6 points, whereas the fourth 0.05 per cent increment depressed it by only 1.5 points—a factor of 4. Although the first increment (0.05 per cent sulfur) more nearly represents the average amount of disulfide sulfur that is to be found in cracked naphthas because of the conversion of the mercaptans into disulfides, nevertheless it is misleading to assume that the effect of the disulfide sulfur on the sulfur-free gasoline would be the same as its effect on cracked naphtha relatively rich in organic sulfur (*e.g.*, from 0.10 to 0.75 per cent) other than mercaptan or disulfide sulfur. No information now available seems to indicate that this small increment of disulfide sulfur would affect the octane number very much more than a corresponding increment of any other organic sulfur except a polysulfide. It must be remembered that it is only when the total sulfur content is very low (from 0 to 0.05 per cent) that small changes in the sulfur content, regardless of the type of sulfur, greatly modify the lead susceptibility.

Since all sulfur in gasoline adversely affects lead susceptibility and since each increase of one point in octane value in the range of 74 to 80 costs the refiner about five cents per barrel of gasoline,²⁴⁴ the desirability of any method that will lower the sulfur content becomes more apparent.

Applicable to the subject of sulfur removal and lead susceptibility is Table 22 of Chapter II, page 94, from the work of Graves.¹¹⁹ Three samples of a given cracked gasoline stock were refined with different amounts (10.5, 21.0, and 31.5 lbs. per bbl.) of 98 per cent sulfuric acid at 20° F. Each treated product was examined for sulfur content, octane rating, and lead susceptibility; and finally the two more heavily treated samples were examined for octane rating and lead susceptibility when organic sulfur compounds were added to them in sufficient quantity to duplicate the sulfur

content of the preceding less heavily treated stock. The successive heavier acid treatments slightly lowered the octane numbers of the unleaded gasolines but raised their susceptibility to lead. When the pure organic sulfur compounds were added, no detectable effect on the knock rating of the unleaded samples was found, but the poorer lead susceptibility of the higher sulfur content stock was duplicated.

Henderson, Ross, and Ridgway¹³³ find that extracting a large proportion of the mercaptans from the sour gasoline by countercurrent caustic washing increases the lead susceptibility over that of the sour naphtha because of the decrease of the sulfur content of the gasoline. The Solutizer process, described later, removes the mercaptan sulfur and yields higher lead susceptibility.

Laboratory Examination of Sodium Plumbite Solution for Refinery Control

The sodium hydroxide content of the doctor solution can be determined by titration with acid, phenolphthalein and methyl orange being used as indicators.⁵⁵ This method is not strictly correct when applied to a spent doctor solution containing accumulated phenols and organic acids, but there is no other convenient method available leading to more reliable results. The lead is precipitated during the titration, and corrections for it should be made on the basis of an analysis of the lead in the solution.

The lead content is determined accurately either gravimetrically or volumetrically, or roughly by centrifuging. Gravimetric determinations are slow, and the volumetric method gives the same degree of precision. In the latter, ammonium molybdate is used to precipitate the lead, tannic acid being used as an outside indicator.²¹⁶ In the centrifuge method, measurement is made of the volume of lead chromate produced by precipitating the lead with potassium dichromate, and then centrifuging.⁷ This last method is considerably less accurate than the other two and is used only when a large number of samples is to be analyzed in a short time and when great accuracy is not required. For quick testing of a qualitative nature, the lead can be precipitated with sodium sulfide solution.⁵⁵

Preparation of Commercial Reagents

The commercial sodium plumbite solution is made in the refinery by dissolving litharge in an aqueous solution of sodium hydroxide. The concentration of the sodium hydroxide solution usually runs from 6° to 30° Bé. (about 4 to 24 per cent).⁸⁹ Morrell¹⁷⁴ prefers the use of a higher concentration if the doctor treatment precedes the acid treatment than if it follows; for example, 13.5 to 24 per cent sodium hydroxide solution is

recommended before the acid treatment, and a 4 to 11 per cent (6° to 16° Bé.) solution after it.

Very high concentrations of caustic are usually not recommended because of emulsification losses. This rule applies primarily when water-washing the oil follows soon after the treatment with doctor solution. In tests on the rates of settling of alkaline solutions of different concentrations for a relatively short period of time, the volumes of the solutions remaining suspended in the oil are usually approximately the same, and the actual amount of alkali lost is proportional to the concentration of the alkali solution. In many specimens of gasoline the alkali settles out in several hours and leaves the oil neutral to phenolphthalein indicator. Low concentrations of caustic may be objectionable in that more of the solution is needed for the same volume of gasoline; and, furthermore, the weak caustic soda solution may not remove so completely the weak acidic constituents from the oil if this removal is attempted simultaneously with the doctor treatment.

Unless the oil is given a preliminary washing with caustic soda solution, the doctor solution may quickly become contaminated with various organic acids and phenols; and if the solution is repeatedly fortified and re-used, it may cause discoloration of the oil and rapidly lead to heavy emulsifications.

The lead oxide, or litharge, should be dissolved in the caustic soda solution before the solution is brought into contact with the oil, as only the litharge which is dissolved is reactive. The solubility of litharge in caustic solution is variable, depending on the grade used, the strength of the alkali solution, and the temperature. The data on the solubility found in the literature are, therefore, not always in agreement. On the average, about 1.5 per cent of litharge (by weight) dissolves in a 16° Bé. (11 per cent) sodium hydroxide solution, and about 3.0 per cent in a 30° Bé. (24 per cent) solution;^{89, 129, 174} but as much as 6 per cent of litharge may dissolve in a 10 to 12 per cent sodium hydroxide solution at a temperature a little below 212° F. The solubility of litharge in caustic increases with the concentration of the sodium hydroxide up to a maximum in a 25° Bé. solution and then begins to decline.¹²⁶ In the place of litharge, other salts of lead can be used.¹³⁵

Rhombic, or lump, sulfur is used in doctor treatment if sulfur is required. Sulfur which is highly soluble in the oil should be selected. Flowers of sulfur are not sufficiently soluble. It is more convenient and often preferable to dissolve the sulfur in a small fraction of the oil and blend this fraction with the main portion of the oil, since such an operation permits measuring the volume of the solution rather than weighing the solid sulfur. It is convenient to deflect a small stream of gasoline, if continuous treatment is used, upward through a tower containing roll sulfur and then to

inject this stream of gasoline and dissolved sulfur into the main stream before or after the latter is contacted with the doctor solution.

Normally, gasoline dissolves from 0.3 to 0.5 per cent by weight of rhombic or roll sulfur, but under certain circumstances it dissolves as much as 1.5 per cent of the sulfur.^{122, 174} The solubility of the sulfur increases with increase in the molecular weight of the oil and with rise in the temperature.^{80, 111} On cooling, the excess sulfur crystallizes out. At high temperatures sulfur acts chemically on oils (also on prolonged standing at room temperature). Hydrogen sulfide and organic sulfur compounds soluble in the oil are formed.

Refinery Operation

Sour distillates can be treated with plumbite solution by the batch or preferably by the continuous process.* The latter has its usual advantages. Air agitation or the addition of a little air has some advantage over straight mechanical agitation because of the fact that it regenerates by oxidation the lead sulfide formed in the sweetening reaction, and it greatly lessens the amount of sulfur required since it also oxidizes some of the mercaptans. It is usually advisable to combine air and mechanical agitation, the minimum amount of air being used to effect the desired oxidation.

The Standard Oil Development Company²⁹¹ and Fischer¹⁰¹ sweeten heavy naphtha, kerosene, etc., by agitating with litharge and sodium hydroxide solution in the presence of air or an oxygen-containing gas. Sulfur is added during the sweetening. For further data on the influence of air on reducing the amount of sulfur and lead required for sweetening, see publications by Rowsey and Whitehurst²⁰⁰ and by Lachman.¹²³

It is often the better practice to introduce the sulfur into the sour gasoline before the gasoline is agitated with the plumbite solution, but some investigators^{93, 132} find, for certain naphthas at least, that less sulfur is needed if the sour naphtha and plumbite are commingled first and the sulfur added afterward.

Emery⁹³ has described the present operation of the plumbite sweetening process of the United Refining Company, which is illustrative of a very practical method of handling doctor sweetening. The sour gasoline and plumbite solution are thoroughly mixed by first being passed through two Duriron mixers in series and then through a series of five eight-foot vertical pipes. Each of these pipes contains baffles that cover about two-thirds of the cross-section of the pipe and are spaced at two-foot intervals. As the gasoline-plumbite mixture leaves these pipes, the sulfur is added by introducing a small proportion of the gasoline which has been by-passed through a tower of sulfur. The sulfur-oil-plumbite mixture is mixed in a zigzag passage through pipes provided with mixing aids, and then delivered into a settling drum. The sweetened gasoline is then water-washed and passed through a sand filter.

* Both processes are discussed by Hallett and Sowers.¹²⁰

In one patent sour naphtha is warmed to about 85-100° F., sulfur solution injected into it while it is flowing in a pipe, and the mixture passed through a tower of sodium plumbite solution. The treated gasoline overflows from the top of the tower.⁴⁴

Lowry, Dryer, Wirth and Sutherland,¹⁶² in describing desirable technique in plumbite sweetening, have shown that better results are derived from the use of sweet rather than sour gasoline to dissolve the sulfur which is to be added to the plumbite-sour naphtha mixture. They point out the desirability of sweetening the naphtha at a temperature of 85° F. or higher.

It seems certain that different stocks respond differently to the order in which the sulfur and the plumbite solutions are added; and because of the importance of adding the least possible proportion of sulfur, the refiner should determine the proper order of the additions.

Volatile products, such as natural gasoline, can be blended with a heavier product before the sweetening to minimize evaporation.⁸⁸

Gasoline of greater color stability is obtained with some stocks if a little sodium sulfide, formed by washing gasoline containing hydrogen sulfide with sodium hydroxide, is added to the doctor solution, and the mixture then applied to the gasoline under air agitation.²⁰⁹

Claims are made that cracked oil can be advantageously agitated with doctor solution, and an aqueous solution of sodium polysulfide added to the treated oil to release elemental sulfur and hasten the precipitation of the lead; but the practicality of this procedure is doubted.²³⁹

For better subsidence of the lead compounds in sweetening, the addition of a little fuller's earth or clay has been used.²⁸ However, washing with water or the addition of a little sodium sulfide is usually effective.

In the plumbite treatment the consumption of the reagents is variable. In treating natural gasolines, 1 to 2 per cent by volume of doctor solution is usually used, and about 0.02 to 0.2 pound of litharge is converted to the sulfide per barrel of oil.²³⁰ Similar figures apply to other grades of gasoline.^{89, 174}

The losses of oil in the treatment vary and may run from a fraction of a per cent up to one per cent, depending on the amount of emulsion formed and the evaporation.

When sulfuric acid is used in the refining of cracked gasoline, the complete treating operations are usually as follows:

- (1) Contacting the gasoline with the acid, preferably in a continuous operation. If much acid is used, as may be required in reducing the sulfur content, the acid is frequently added in increments, the mixture being cooled between the increments, and the acid sludge separated as quickly as possible.

- (2) Washing the gasoline with water.

- (3) Washing the gasoline with aqueous caustic soda solution.
- (4) Steam-distilling the gasoline with good fractionation to give "end point" gasoline.
- (5) Treating the gasoline with doctor solution and sulfur by adding the sulfur to the gasoline stream, then adding the plumbite solution, and separating the aqueous solution from the gasoline.
- (6) Washing the gasoline with water until free of lead sulfide.

Sweetening Before Acid Treatment or Before Distillation

The sodium plumbite may precede or follow acid treatment^{107, 176, 178} or distillation. When acid is used, it is the usual practice to sweeten after acid treatment and distillation, for if sweetened before distillation, the gasoline may turn sour during distillation unless the temperature is kept relatively low by the use of ample steam or a vacuum. The product has a higher octane number and greater chemical stability if the gasoline is sweetened before rather than after distillation provided the gasoline can be kept sweet during distillation. Polysulfides formed in the sweetening do not distill over, and as the alkyl disulfides have higher boiling points than the original mercaptans, they tend to remain behind in the still. (See Table 34, page 186.)

Table 39. Comparative Octane Rating of Gasoline Sweetened Before and Sweetened After Distillation.

East Texas Naphtha	Sour Naphtha	Sweetened and Rerun to 10 Per Cent Bottoms	Rerun to 10 Per Cent Bottoms and Sweetened
Gravity (° A.P.I.)	58.0	58.5	58.5
A.S.T.M. Distillation (° F.)			
I.B.P.	104	103	104
10%	164	161	162
50%	248	233	234
90%	336	324	322
E.B.P.	398	382	385
Recovery (%)	98.0	98.0	98.0
Reid Vapor Pressure (lbs./sq. in.)	5.2	4.4	4.4
Doctor Test	+	O.K.	O.K.
Corrosion Test	O.K.	O.K.	O.K.
Sulfur (%)	0.038	0.038	0.039
Octane Number, C.F.R.	61.3	66.4	62.5

The effects of sweetening before and sweetening after distillation are compared in Table 39. A straight-run naphtha of relatively low sulfur content was used.²⁶³ Sweetening before rather than after distillation gave a gasoline of over three points higher octane number.

Morrell and Egloff¹⁷⁸ point out that sweetening sour gasoline before acid treatment gives a lower sulfur content than acid-treating first and then

sweetening. This effect is evident from the early experiments of Wood, Lowy, and Faragher²⁰⁰ and Birch and Norris,²⁶ who observe that disulfide sulfur, the product of sweetening, is more easily extracted from gasoline by concentrated sulfuric acid than is mercaptan sulfur.

It is the usual practice for refiners to treat with acid before sweetening because the acid oxidizes some of the mercaptans into other oil-soluble sulfur compounds, and consequently in the subsequent sweetening there is less formation of lead sulfide and emulsions with less loss of gasoline. Since some of the present methods of sweetening avoid emulsion formation, sweetening before the acid treatment may be practical and economical.

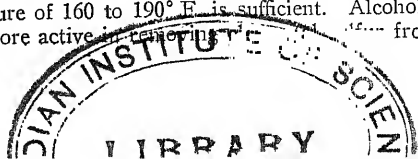
It is well known that distilling after acid treatment raises the octane rating and lead susceptibility of gasoline. Hebl, Rendel, and Garton¹³¹ point out that the effect is due to the elimination of disulfides and other sulfur compounds.

Treatment to Correct Corrosiveness

Corrosiveness in a finished gasoline can nearly always be ascribed indirectly, and sometimes directly, to elemental sulfur. This can be removed by adding mercaptans and then treating with sodium plumbite solution. Pure mercaptans can be added to the gasoline;^{15, 254} or sour gasoline, such as adsorption gasolines from cracking processes, which are rich in mercaptans, can be added.¹⁹⁰ If both products are available in the refinery, it is economical to mix in proper proportions a sour gasoline with one containing corrosive sulfur and then treat the mixture with the plumbite solution.¹⁴⁰ A modification consists in treating a petroleum distillate containing elemental sulfur with a doctor solution which has already been used to treat a sour gasoline containing mercaptans or mercaptans in excess over the elemental sulfur, and which can absorb a little more sulfur.²²² This treatment for removing elemental sulfur is essentially the same in chemical reaction as the doctor treatment, and no further discussion of it is required.

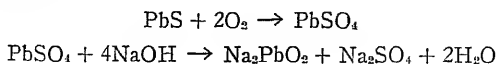
The treatment of oils with a water solution of sodium sulfides is intended primarily for the removal of elemental sulfur. Birch and Norris²³ report that it is possible to sweeten some oils by converting the mercaptans to disulfides by the oxidizing action of sodium polysulfide and sodium hydroxide at elevated temperatures.

The washing of cracked distillates after doctor treatment with an aqueous solution of sodium sulfides and polysulfides at 80 to 86° F. is patented for the removal of any active sulfur added in excess of the requirements during sweetening.^{175, 230} A concentrated and strongly alkaline solution of sodium sulfide is necessary for this purpose.²³ Potassium and the alkaline-earth sulfides and polysulfides can also be used.¹⁰² To free the oil of elemental sulfur, it is agitated with the alkaline sulfide solution for as long as five or six hours at 100° F., then washed with dilute sodium hydroxide solution, and finally washed with water. According to Cobb,⁵⁸ agitation of from one to three hours at a temperature of 160 to 190° F. is sufficient. Alcoholic solutions of the alkali sulfides are much more active in removing sulfur from oil than are aqueous solutions.



Regeneration of Sodium Plumbite Solution

The spent doctor solution contains unused sodium hydroxide and lead sulfide; a simple method of utilizing the chemicals is to add more litharge to the solution and carry the lead sulfide in suspension, since the latter aids the sweetening if an ample supply of oxygen (air) is provided. Modifications of this process are in use in many refineries. Much more commonly, however, the spent doctor solution is regenerated several times by the atmospheric oxidation of the lead sulfide to plumbite in hot caustic soda solution. The operation is rather complex because of the emulsification of the oil and alkali solution by the lead sulfide and accumulated by-products, such as phenols. The lead sulfide is oxidized to lead sulfate (and possibly lead thiosulfate), which is instantly converted into sodium plumbite by the caustic soda in the following manner, as discussed previously on page 189.



The concentration of the sulfate ions in the first few regenerations is low, and the lead dissolves as the sodium plumbite. However, after further regenerations, the sulfate ion increases to a point at which the lead sulfate will no longer dissolve, and then the aqueous solution of alkali sulfate and other products are separated as well as possible from the insoluble lead salt, and the lead salt is redissolved in fresh caustic under atmospheric oxidation.

The method used by the Atlantic Refining Company^{12, 93} for regenerating its doctor solution is illustrative of one procedure. That refinery recovers daily about 17,000 pounds of litharge, 55,000 pounds of 11 to 13 per cent caustic soda solution, and 450 barrels of oil from its spent doctor solution. The spent solution, consisting of 0.6 per cent litharge in solution as plumbite and more than 4 per cent of lead sulfide in suspension in the 11 per cent caustic solution, is stored in one of two 85,000-gallon storage tanks. The oil which separates here is sent to storage; the middle layer, or emulsified caustic and naphtha, contains the lead sulfide and is taken to a "break tank"; the bottom liquid, the sodium plumbite, is drawn off to temporary storage. The charge in the break tank is heated gradually by steam coils to about 150° F., a process which causes it to separate into three layers: oil on top, a caustic solution in the middle, and a slurry of lead sulfide at the bottom. The oil is drawn off. The sulfide suspension is pumped to blow tanks, heated to 175° F., and blown with air passed through perforated tubes, which radiate from a header at the bottom of the tank. For each pound of litharge recovered, 130 cubic feet of air is used. The regenerated doctor solution is decolorized by washing with oil by means of

an orifice plate mixer, consisting of five sections of 12-inch pipe, each 18 inches long, separated by plates, each with a 3-inch hole in it, placed eccentrically.

It is usually possible to continue such regenerations if some of the caustic of the spent doctor solution (10 to 20 per cent of the total) is withdrawn and used as a precaustic wash for the gasoline and then discarded and an equivalent quantity of fresh caustic soda added to the remainder of the doctor solution. A small amount of litharge is also added to supplant the inevitable loss. However, for some cracked products the doctor solution cannot be thus revived so satisfactorily, since the accumulation of coloring matter injures the color and chemical stability of the distillates with which the revived doctor solution is brought into contact. The solution also accumulates cresols, phenols, and organic acids, which produce soaps with the alkali. These soaps have strong emulsifying tendencies and prevent the plumbite solution and sulfides from settling from the distillate. Under the most favorable conditions, the precipitated lead sulfide emulsifies so completely an appreciable amount of the distillate that it will not settle out for days. This behavior can readily be shown in the laboratory by agitating in a 100-cc. centrifuge tube 100 cc. of the sour distillate and the proper quantity of dissolved sulfur with a definite volume of doctor solution, *e.g.*, 5 cc., and letting subsidence take place by gravity. In moderately sour California cracked distillate, the volume of the plumbite solution plus the emulsion will be from 6 to 7 cc., even after 24 hours, a quantity which shows an emulsification of from 1 to 2 per cent of the gasoline.

Many refiners now subject the highly emulsified portion ("black strap") of the spent doctor solution to continuous centrifugal separation; the products are gasoline and lead sulfide, the latter containing as little as one-half per cent of gasoline. In the absence of oil the lead sulfide is oxidized much more readily by air.

Berger¹⁸ describes a centrifuge installation in a refinery of the Globe Oil and Refining Company of Kansas and submits data on the quantity of gasoline recovered by the centrifuge which otherwise would be lost. Because of the separation of the oil from the spent doctor solution, it is possible to reoxidize the lead sulfide at 120° F. instead of the usual 165-190° F. A high concentration of dissolved lead is maintained by recirculating the partly regenerated plumbite solution through the air oxidation unit and by replacing the exhausted caustic soda with fresh material.

The rate at which the lead sulfide in the doctor solution can be reoxidized by air is variable. Organic impurities (*e.g.*, phenols) lower the rate either by inhibiting the oxidation or by adsorption on the lead sulfide, thereby excluding the oxygen. The rate is also influenced by the temperature and by the amount of oxygen (air) dissolved in the plumbite solution; the concentration of the oxygen is decreased with rise in temperature and increased

with air pressure. To increase the concentration of oxygen, some refiners apply the air under pressure of 20 to 75 pounds,^{2, 77} preferably by pumping the hot lead sulfide-caustic soda and air upward through a vertical tower and delivering the mixture from the top of the tower to the bottom of a receiving tank where it is released into the tank through a perforated coil. Under favorable conditions the time of contact can be reduced from 10 to 15 hours to about 2 hours. In fact, Dunham⁷⁷ found it possible to increase the rate of oxidizing lead sulfide at 150° F. eighty-fold by increasing the air pressure from atmospheric to 100 pounds per square inch. Dunham also found that the temperature for the maximum rate of oxidation in open tanks (atmospheric pressure) is 150° F., but with 100 pounds pressure, it is about 275° F. An increase in the quantity of suspended lead sulfide increases the oxidation rate.

The lead sulfide dissolves faster in the caustic solution if there is at least 2 pounds per barrel of dissolved lead (PbO) in the solution; for that reason the doctor solution is removed from the treating system and regenerated when the dissolved lead is depleted to about 2 pounds per barrel.⁹³

Wilson²⁵⁷ accelerates the rate of reoxidizing the lead sulfide in the spent doctor solution by adding a small amount of hydrogen peroxide to the solution. As an average behavior, the addition of 40 pounds of 28 per cent hydrogen peroxide to 230-250 barrels of spent doctor solution increases the rate of oxidation of the lead sulfide by a little over 60 per cent. The peroxide "activates" the solution, probably by oxidizing a film of organic material adsorbed by the lead sulfide, a film that protects the lead sulfide from the air. The peroxide also can oxidize the lead sulfide directly, although the amount of oxidation is too small to be an appreciable factor.

Other methods of regenerating the plumbite solution have been advocated. The lead sulfide can be regenerated into soluble plumbite solution by treating it with hot sulfuric acid and dissolving the resulting lead sulfate directly in caustic soda solution;¹⁵³ or the lead sulfide can be oxidized by chlorine in the presence of water to litharge and sulfur;¹⁰⁰ or the spent doctor solution can be treated with such substances as calcium chloride in order to break up the emulsion, and the precipitate, containing lead sulfide, smelted and the lead recovered.²²⁵

The caustic solution can be regenerated separately by one of the methods which are described in the chapter on Alkali Treatment.

The spent lead, as lead sulfide, can be settled or centrifuged from the doctor solution and re-roasted^{138, 203} at about 900-1100° F., a temperature suitable for oxidation without sintering. Schenck²¹³ has reported the chemical equilibrium between the lead sulfide and its products in the roasting process.

Valentine and MacLean²⁴³ have calculated the quantity of by-product chemicals available from a typical spent doctor solution discarded at the end of ten cycles. The data of Table 40 are based on the use of 10,500 gallons of plumbite solution with an assumed loss and make-up of 5 per cent of the solution each cycle.

Table 40. By-Product Chemicals from 10,500 Gallons of Spent Doctor Solution.

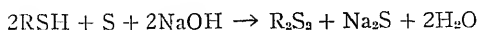
Chemical	Pounds
Na_2PbO_2 (as PbO)	440
NaOH	5050
$\text{Na}_2\text{S}_2\text{O}_3$	8510
Phenolates	8020 ^a
NaCl	130
Na_2CO_3	240
Na_2SO_4 and Na_2SO_3	1600

^a A precaustic wash would extract the phenols in advance of the doctor sweetening.

Sweetening with Sulfur and Alcoholic Solution of Caustic Soda

Stagner²²⁸ has shown that the mercaptans of sour gasoline are converted instantly into disulfides in contact with elemental sulfur and caustic soda-methanol solution with complete avoidance of emulsions. About one quart of commercial methanol containing about 15 per cent by weight of caustic soda is required per barrel of gasoline that contains 0.05 per cent mercaptan sulfur.

The simplest expression for the conversion of the mercaptans is:



However, the reaction is more complex; in addition to the sodium sulfide, some sodium polysulfide and sodium thiosulfate are formed. The sodium reaction products are soluble in the methyl alcohol and settle from the gasoline as a sharply defined liquid layer. An excess of about 20 per cent caustic soda is needed. The excess can be utilized later for neutralization purposes or as a prewash to remove hydrogen sulfide. The methanol can be recovered without a loss of over 0.2 per cent in each cycle.*

This method is recommended for sweetening sour gasoline before the acid treatment or before the redistillation to effect greater sulfur reduction without emulsion losses of the gasoline.

Sweetening with Sulfur and a Powdered Mixture of Litharge, Hydrated Lime, and Caustic Soda

Cannon⁵³ modified the older method of sweetening with the aqueous sodium plumbite solution by substituting for the solution a reagent in the solid state containing litharge, hydrated lime, caustic soda, and preferably about 22 per cent of pulverized diatomaceous earth, the earth to effect and

* The recovery of 99.8 per cent of methanol from light oils has been confirmed by Brandt and Hougen.⁴¹

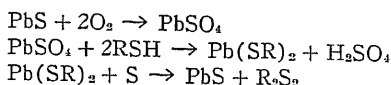
maintain a better degree of contact and to simplify filtration in the last stage of the operation. The total time of contact between the oil and solid reagent is from 3 to 7 minutes. Elemental sulfur is used, as in the sodium plumbite sweetening. An example of the approximate proportions of ingredients given in parts per hundred in the sweetening reagent is:

Sodium hydroxide	3
Calcium hydroxide	25
Litharge	16
Diatomaceous earth (200 mesh)	22
Moisture	34

The reagent is prepared by adding the hydrated lime to a caustic soda solution of proper dilution to make a cream-like emulsion, adding litharge and further mixing, and finally mixing thoroughly with the diatomaceous earth, the product being a damp but slightly coherent powder. The preferred method of treating the oil with this powder is by a continuous operation in which the oil is first pumped in an upward direction through one tower containing a loose mass of partly spent reagent, the rate of flow being such that it permits most of the reagent to settle from the oil before the oil overflows from the tower. The oil then passes downward through a bed of fresh reagent in a second tower, the process being one of combined "contact" and filtration. The failure to maintain a high filtering rate has militated against the use of this method.

Sweetening with Dry Lead Sulfide, Air, and Sulfur without Caustic Soda

A bed of dry lead sulfide as catalyst deposited on a porous carrier, such as clay, boneblack, or activated alumina,^{128, 129} sweetens a stream of sour gasoline when both air and the proper amount of sulfur are present. Accurate measurements show that four atoms of oxygen are used to one of sulfur, a ratio indicating that the oxygen may be converting the lead sulfide to lead sulfate, which with the aid of the sulfur oxidizes the mercaptans. The following chemical reactions are suggested:



The second equation indicates the formation of sulfuric acid, although none could be detected.

The dry lead sulfide and sulfur without oxygen would not sweeten the gasoline, although the lead sulfide and oxygen without sulfur sweetened the gasoline for a short time and then ceased to sweeten.

In pilot experiments, the sweetening continued for 94 hours until an accumulation of gummy material adsorbed on the lead sulfide catalyst

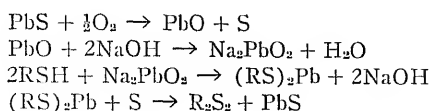
retarded the reaction to the extent that only three-fourths of the mercaptans were converted. The catalyst was restored by extraction of the gum. The inventors of the process believe that its practicability depends on preventing trouble from the adsorption of the gum by the catalyst.

The process would obviate the use of caustic soda, the formation of emulsion, loss of naphtha, and the periodical regeneration of a spent solution.

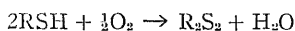
Sweetening by Means of Lead Sulfide and Air without Elemental Sulfur

In experiments on the regeneration of spent sodium plumbite solution, it had been observed^{4, 124, 179, 209, 234} that the presence of lead sulfide in sodium plumbite very often facilitates the sweetening operation; this behavior led to a study of the possibilities indicated. As a result, it has been found that the use of lead sulfide in a suspension in caustic soda solution greatly simplifies the sweetening procedure and eliminates the actual chemical consumption of litharge, caustic soda, and sulfur.

The following chemical reactions are suggested in the literature as representing the steps in sweetening with lead sulfide in caustic soda solution with a limited amount of air:



The four preceding equations may be summarized more simply thus:



The lead sulfide and caustic soda enter into the sweetening; but both are regenerated, and only the oxygen is consumed.

This process operates in a closed system in a continuous manner and consists in intimately contacting the sour gasoline with preformed, dense, and quick-settling lead sulfide which is suspended in a strong caustic soda solution. To this mixture is usually fed a very small, positively regulated quantity of air to activate the lead sulfide reagent. If the naphtha has only a little mercaptan, the naphtha may contain sufficient dissolved air (oxygen) for the sweetening. If it is necessary to add supplementary air,* it is extremely difficult to control the quantity to the theoretical amount required. Any excess air, therefore, converts some lead sulfide to sodium plumbite in the presence of caustic soda, as indicated by the foregoing reactions, and interferes with the sweetening reaction. In order to counteract this effect and maintain the reagent in the substantially balanced condition

* The volume of air is usually less than 0.15 cu. ft. per barrel of gasoline; but for high mercaptan content stock, it may be as much as one cu. ft. per barrel.¹⁸²

required for successful sweetening, it is necessary to add continuously a small, regulated quantity of aqueous solution of sodium sulfide[†] to the system. The sodium sulfide re-precipitates the sodium plumbite as lead sulfide.

The data of Table 41¹⁸² represent the maximum requirements of chemicals to sweeten a barrel of sour gasoline.

Table 41. Chemicals Consumed per Barrel of Gasoline Sweetened.
Pounds per Barrel.

% Mercaptan Sulfur	0.01	0.02	0.03
Sodium Sulfide	0.03	0.06	0.09
Litharge	0.0077	0.0085	0.01
Caustic Soda ^a	0.0077	0.0085	0.01

^a Net consumption of caustic after credit is given for diluted caustic withdrawn from the system.

The lead sulfide process is more economical than the plumbite sweetening. Since no elemental sulfur is added, there can be no increase in the total sulfur and no formation of alkyl polysulfides. The sweetened gasoline has a higher lead susceptibility than the plumbite-sweetened gasoline. The reagent is not regenerated by air-blowing, as necessary with spent doctor solution, although in time the lead sulfide adsorbs a film, apparently of phenol-like substances, that lowers its activity. The lead sulfide is then regenerated by settling and separating it from the aqueous solution and washing it free of the film with hot water.

The process is patented²⁰⁸ and is now in commercial operation in several refineries. It is licensed by the Stratford Development Corporation of Kansas City, Missouri.

Investigations show that lead sulfide adsorbs and holds some of the sulfur compounds present in the oil, such as alkyl sulfides and mercaptans. Henriksen^{121, 134} observed that the oil extracted from lead sulfide, formed in the doctor treatment of a certain gasoline, contained 0.363 per cent sulfur, whereas the treated oil had a sulfur content of less than 0.10 per cent.

It is claimed by Low¹⁰¹ that sweetening can be economically effected by filtering sour gasoline through air-dried lead sulfide, which can be regenerated by treating with a water solution of a soluble sulfide and again drying with air at about 230° F. He does not use sulfur in the sweetening. Without question, much of the sulfide is oxidized to sulfate during the air drying, but it seems probable that the sweetening may come from the adsorption of the mercaptans, under which condition the lead sulfide could not react catalytically or in the cycle of sulfide to sulfate to plumbite, as described by Morrell and Faragher. Low's patent implies frequent revivification.

Greer¹²¹ reports that the sulfides of copper, lead, cadmium, or arsenic adsorb mercaptans from gasoline and leave the gasoline sweet, the copper sulfide being the most efficient. The experiments were made by agitating in stoppered test tubes the sour gasoline, containing 0.4 to 0.5 per cent of mercaptan sulfur, with the sulfides; but apparently some air was present, and air may also have been present during the preparation and drying of the sulfides, a condition not discussed in the report.

[†] Sodium sulfide is usually a refinery waste product.

Because of the interest in the lead sulfide as a catalyst, different methods have been considered for producing lead sulfide which is active under the conditions required for the sweetening reactions. Rather²⁰² produces it by passing hydrogen sulfide into water-soluble lead salt solution. Guthrie¹²⁴ describes the method of digesting litharge with a sodium sulfide solution. The sodium sulfide can usually be obtained by washing the oil, preliminary to other treatment, with sodium hydroxide solution.

Treatment with Cupric Sulfide

Amorphous cupric sulfide adsorbs mercaptans and can be used for sweetening gasolines. It is better in this respect than stannic, cadmium, or arsenious sulfides, which also adsorb mercaptans but require more time.¹²¹ Adsorption of mercaptans with copper sulfide and other solids, such as litharge, lead sulfide, mercury salts, iron, antimony, zinc, kieselguhr, silica gel, etc., has been studied in considerable detail.²²³ None of these substances can replace the treatment by doctor solution because of the extra costs, difficulty of handling, etc.

Treatment with Cadmium Sulfide

Cadmium sulfide is claimed to catalyze the decomposition of mercaptans in the vapor phase. At the higher temperatures the mercaptans are decomposed into hydrogen sulfide and an unsaturated hydrocarbon.²¹¹ This procedure apparently has never been given practical application.

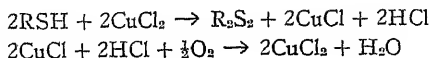
Treatment with Cadmium Hydroxide

Cadmium hydroxide suspended in an aqueous solution of sodium hydroxide is recommended for removing mercaptans from cracked gasolines.³⁰ The separation of the reagent from the oil is effected by filtering through fuller's earth. According to the patentees, the cadmium hydroxide removes mercaptans and sweetens the gasoline but does not attack other sulfur compounds in the oil.

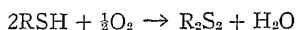
Sweetening with Copper Salts without the Aid of Elemental Sulfur

Cupric chloride is now in extensive use to oxidize the mercaptans of light oils to disulfides and thus sweeten the oils. The copper salt becomes reduced to the cuprous salt but is reoxidized by air at normal temperatures, the regeneration being simultaneous with the conversion of the mercaptans if dry, or solid, copper salt is used, or a separate operation if an aqueous solution of the copper salt is used. Some individual refiners use both the solid and the liquid processes.

The chemical reactions in the sweetening and regeneration are:



As the cupric salt is fully restored, the oxidation of the mercaptans can be summarized by the equation:



A sour naphtha that is distinctly stable chemically (straight-run or natural gasoline) is preferably sweetened by filtration in contact with a little air in continuous operation through a bed of adsorbent material, such as fuller's earth,⁹ impregnated with the copper salt. In this manner the mercaptans are converted to the disulfides, and the copper salt reoxidized simultaneously without the need of a separate regeneration step. However, a sour naphtha that is chemically unstable (cracked gasoline) and that is deleteriously affected by air in contact with the copper salt is commingled in absence of air in continuous operation with an aqueous solution of the cupric salt, and the spent aqueous copper solution is regenerated in a separate tank by air oxidation. The cracked naphthas treated with the copper salt solution are finally washed with sodium sulfide²¹⁹ or some similar reagent to stabilize their color and resistance to gum formation by removing minute traces of copper which would otherwise act catalytically in degrading the oil.

Hydrogen sulfide is always removed from the sour naphtha by an alkaline wash before the copper sweetening; copper sulfide cannot be regenerated to an active sweetening agent by atmospheric oxidation.

The dry fuller's earth-copper salt is not corrosive to metal and is used in ordinary equipment; but the aqueous copper salt solution is corrosive to iron and steel, and it must be used in corrosion-resisting material, such as wood, or iron coated or lined with a non-corrosive material.

The copper sweetening process avoids the use of elemental sulfur, the troublesome emulsions, and the wasteful regeneration operations of plumbite sweetening.

There are three principal copper sweetening processes: Perco (Perco, Incorporated, Bartlesville, Okla.), Universal Oil Products (Universal Oil Products Co., Chicago, Ill.), and the Linde (The Linde Air Products Co., Carbide and Carbon Chemicals Corp., New York City).

Van Voorhis²¹⁶ has described several of the copper sweetening installations; other details of the process are described in the literature.^{1, 220, 221}

Treatment with Copper Sulfate

Cupric sulfate has been known for many years as a reagent for desulfurizing and deodorizing oils. According to Sommer,²²⁷ the oil can be partly desulfurized by digesting with dry copper sulfate at about 270° F. With some oils mere agitation with a water solution of copper sulfate,⁶ or with an alkaline solution containing the hydroxides of copper,⁵ is sufficient. Hydrogen sulfide is preferably removed with caustic soda before treatment

with copper sulfate. The mercaptans are converted into copper mercaptides or oxidized by the copper salt to alkyl disulfides.

The boiling of crude oil with 5 per cent of a solution of copper sulfate, sodium hydroxide, and sodium chloride (one part of salts to 18 parts of water) was also early suggested for the removal of odors. The salts were then washed from the oil, the addition of sulfur to aid in their separation being optional.¹⁵¹

Copper sulfate has been used for removing malodorous and resinous substances from cracked distillates.¹⁵⁰ A solution of cupric ammonium hydroxide, formed by pouring a cold solution of copper sulfate into a cold solution of sodium hydroxide and adding a slight excess of ammonium hydroxide, is also used in treating pressure distillates, and it is claimed that this method has some advantages over the treatment of oils with doctor solution.¹⁴³ One patent recommends treating gasoline by agitating it first with ammonium chloride and then with copper sulfate and zinc sulfate.²⁵⁰

Hypochlorite Treatment

The direct use of chlorine for treating oils had been recommended prior to the use of hypochlorites, but was abandoned because the oil became chlorinated.⁸⁷ Experiments were made with free hypochlorous acid, or, indirectly the same thing, with chlorine dissolved in water; but these methods were also impractical because of chlorination of the oil. As early as 1889, patents were issued for the use of solutions of chlorinated sodium or potassium hydroxides for treating oils,¹²⁰ and in 1903 a patent was issued for the desulfurization of petroleum distillates by means of a hypochlorite in alkaline solution. The excess chlorine was claimed to be removed from the oils by a salt of a heavy metal which is capable of existing in two or more states of oxidation, such as manganous or ferrous salts.⁶⁰

Colin and Amend⁶⁰ describe the use of an alkaline solution of hypochlorous acid to which catalysts, such as salts of iron, copper, nickel, cobalt, or manganese, are added. The process consists in agitating the oil with a solution of sodium or calcium hypochlorite in the presence of a very small amount of manganous nitrate. The manganous dioxide formed acts as a catalyst in speeding up the reaction.

The commercial application of the hypochlorite treatment of oils was not at all successful until about 1918, when the chemistry of the process had become better understood, and the importance of maintaining a certain degree of alkalinity in the solution was realized.^{83, 87}

Though sodium hypochlorite and the more popular calcium hypochlorite are the only important reagents of their class now in use, hypochlorites of other metals, such as aluminum, zinc, manganese, iron, or copper, have at one time or another been recommended for the desulfurization and sweetening of oils.³⁵

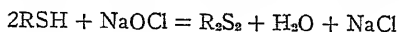
All these processes have been developed primarily to sweeten and desulfurize petroleum distillates, though numerous claims are made that the finished oil is free from gum and stable in color and that it possesses good non-detonating properties. The stability of color, however, is not satisfactory for most of the cracked oils. The color may be good immediately after the treatment; but even on standing only a few days, the oil may darken, and it has a tendency to form gum.

The modern hypochlorite treatment was originally developed in the refining of distillates from Persian crude oils. It is now used on straight-run gasoline in many American refineries, and it is especially recommended for treating natural gasoline or refinery absorption gasolines sour to the doctor test. At present over 80 per cent of natural gasoline sweetened in the oil fields is treated with hypochlorite solutions rather than with doctor solution. The hypochlorite solution is the more easily handled;^{117, 137, 200} and the cost of reagents and loss of oil are less.^{84, 85, 137} The refining can be carried out in steel apparatus, and the total number of mechanical operations is less than in the doctor treatment. Very few heavy, or mediumly heavy, oils can be treated with hypochlorite alone, and sulfuric acid treatment in addition must almost always be used for producing a satisfactory color and reducing the sulfur if the sulfur content is high. The use of hypochlorite for reducing the total sulfur content of an oil is not practical.

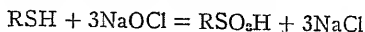
Chemistry of Hypochlorite Treatment

The action of hypochlorite on sulfur compounds depends on the type and molecular weight of the sulfur compounds, the degree of free alkalinity of the hypochlorite solution, the amount of available chlorine, the volume ratio of the hypochlorite solution to the naphtha solution, and the time and intensity of agitation. It does not readily attack all the sulfur compounds, and for this reason any appreciable desulfurization of oils is not possible.

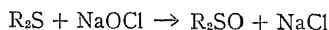
Investigations have shown that the degree of oxidation of the sulfur compounds is variable. The literature is too extensive for complete details here, and the reader is referred to the original articles. Under mild oxidation, mercaptans are converted to disulfides,²⁶⁰ according to the equation:



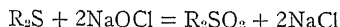
R represents an organic radical, methyl, ethyl, propyl, etc. When the conditions for oxidation are more severe, as with stronger hypochlorite solution, longer exposure, less alkali, etc., the mercaptans and alkyl disulfides, the latter being products of the milder oxidations of mercaptans, are converted into the corresponding alkyl sulfonic acids.^{24, 259} The simplest equation for this oxidation of the mercaptan is:



The sulfonic acids of the low molecular weight hydrocarbons and their sodium salts are soluble in water and are removed from petroleum distillates by washing. The alkyl sulfides, R_2S , when energetically oxidized, first yield sulfoxides,



and on further oxidation yield sulfones,



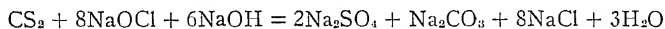
The low molecular weight sulfones, such as ethyl and propyl sulfones, are soluble in water and can be washed from the petroleum products. However, the solubility of the sulfones in water rapidly decreases with increase in molecular weight, and their solubility in oil increases. This phenomenon helps explain the difficulty of removing alkyl sulfides from oils by oxidation and water extraction methods. The same observations would certainly apply to the alkyl sulfonic acids, but to a lesser degree.

The sulfones are not oxidized by an alkaline hypochlorite solution, and they cannot again be reduced to the sulfides.

Elemental sulfur and thiophene are not attacked by alkaline hypochlorite solution.

Hydrogen sulfide is oxidized mainly to water and elemental sulfur, although a little sulfuric acid is formed.²⁴ The elemental sulfur remains dissolved in the oil.

With a large amount of hypochlorite, carbon disulfide is oxidized to sodium carbonate and sodium sulfate, according to the reaction given by Wood, Lowy, and Faragher:



Apparently a small amount of carbon tetrachloride and chloroform are also formed.⁴⁵ The chemical reaction of the hypochlorite solution with carbon disulfide and hydrogen sulfide permits the use of this reagent for the desulfurization of water gas or natural gas.⁴²

Friedmann¹¹² has observed that in treating oils with hypochlorites the speed of oxidation of the sulfur compounds and the solubility of the reaction products in aqueous solution are lowered as the molecular weight of the sulfur compounds increases.

The reports of investigators on the chemical action of hypochlorite solutions on pure sulfur compounds dissolved in naphthas vary greatly because of difference in the conditions of making the experiments. A refiner must keep this fact in mind in trying to interpret the data. An oxidation procedure which would oxidize sulfides to sulfones doubtless

could not be tolerated for use on a cracked gasoline, which is readily discolored, chlorinated, oxidized to yield gums, etc.

A distillation of the oil subsequent to the sweetening lowers the sulfur content, since the sweetening has converted certain sulfur compounds into products having higher boiling points, and these products are left behind in the still. This effect is true for the sulfones produced from sulfides and for disulfides produced from mercaptans. Other compounds, such as alkyl sulfates, produced from the ordinary acid treatment of the distillate, are also left in the still, but they have no particular bearing on the subject of sweetening.

Cracked gasolines sweetened with hypochlorite are often unstable in color and must be redistilled or treated with clay to produce stability. This redistillation after the sweetening is often impractical, since the gasoline usually becomes sour again when redistilled. Because of these factors the hypochlorite sweetening has not become popular in the United States for cracked material, and to the knowledge of the writers it is nowhere in use for this purpose.

Unsaturated hydrocarbons are attacked by the hypochlorite solution, and a process has been developed for utilizing this property in the removal of ethylene and propene from cracking gases.²²⁶ As described later, the chlorination of gasoline can be controlled so that the finished product will be free of chlorine, a condition which is imperative, since the chlorine is capable of doing more damage to an engine than the sulfur compounds.

Other compounds present in gasoline as impurities are to a certain extent attacked by the hypochlorite solution. Alcohols react slowly at room temperature with the hypochlorite solution and rapidly above 120° F.¹⁷¹ Aldehydes and similar substances are also oxidized.

Practical Use of Sodium Hypochlorite Solution

Treatment with sodium hypochlorite solution is valuable primarily for sweetening straight-run gasoline and other light non-cracked petroleum products. According to Gurwitsch,¹²³ the sweetening of heavier oils, even kerosene, is often incomplete. The odor of the higher molecular weight mercaptans (eight carbon atoms or more) is not unpleasant; but these compounds in contact with elemental sulfur are corrosive to metals. Otherwise these high molecular weight mercaptans are not appreciably more objectionable in gasolines than other stable sulfur compounds, such as thiophene or thiophane compounds.

Successful treatment of any distillate with sodium hypochlorite so as to avoid chlorination depends on maintaining within rather narrow limits a certain definite content of free alkali. If the amount of alkali is too low, or especially if the solution is acid, chlorination takes place. The tendency

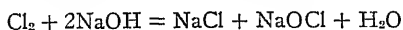
of a given solution to chlorinate the hydrocarbons increases on diluting the solution because of decreasing the concentration of the hydroxyl ions, though the ultimate products of the reaction, with the exception of the chlorination, are about the same with all strengths of solutions.²⁴ If the alkalinity is too high, the time required for the sweetening is impracticably long. The stability of hypochlorite in neutral or in acid solution is rather low. The recommended range of alkalinity of the hypochlorite solution is usually from 0.5 to about 3.0 grams of free caustic soda, or equivalent, per liter (0.17 to 1.00 pound per barrel) of aqueous solution, the range of alkalinity depending on the stability desired for the hypochlorite solution and the tendency of the oil to become chlorinated.^{22, 168} With proper control of the alkalinity there should be no chlorination of the oil. In the treatment of straight-run or natural gasoline the alkalinity produced from a saturated lime solution is shown by Birch and Norris²⁵ to be satisfactory and convenient to use. The stability of a properly prepared sodium hypochlorite solution in a refinery is ample for practical purposes. It has been recommended that the solution be kept fairly alkaline until ready for use, and then its alkalinity reduced just before or during its application to the oil by passing carbon dioxide into it, or by adding salts of certain metals having acidic properties, such as the chloride of iron or the sulfate of iron, zinc, magnesium, etc.²³⁷ The alkalinity of the solution can also be lowered by aeration through the addition of carbon dioxide.²⁷⁰ In general, the solution can be kept in contact with air without harmful effects; and if properly prepared, it need not be protected from carbon dioxide.⁸⁷

Sodium hypochlorite solution for refinery use can be prepared in the following ways:

(1) By double decomposition of calcium hypochlorite solution with caustic soda,¹²⁰ sodium carbonate, or sodium sulfate.²⁷³

(2) By electrolysis of sodium chloride solution.²⁷³ In a modification of this method the sweetening has been accomplished by passing the oil through a brine which is being subjected to the action of an electric current.⁷⁸ The method of the electrolysis of the salt solution has, however, been abandoned in favor of more convenient methods, such as the addition of liquid chlorine to caustic soda solution.^{22, 84}

(3) By direct chlorination of sodium hydroxide. In continuous treatment, chlorine can be introduced into an alkaline solution just before the oil and alkali are brought into contact.¹⁸⁶ The reaction between the chlorine and the sodium hydroxide proceeds according to the equation:



In preparing the sodium hypochlorite stock solution from chlorine and sodium hydroxide solution, Birch recommends that the flow of the chlorine

be steady and that the mixture be well agitated. A temperature up to 110° F. is permissible,²² though 95° F. should be the approximate maximum. The strength of the sodium hydroxide solution used is about 10 per cent, and a cast-iron vessel surrounded by cooling water or containing cooling coils can be used as a container. Chlorine is added until the free alkali is reduced to the desired quantity. This stock solution of chlorine is diluted when needed to about 0.34*N*, a possible working strength, as illustrated by Birch in the following example. Approximately 3000 gallons of the stock solution is prepared by using 2800 pounds of sodium hydroxide, 3000 gallons of water, and 2300 pounds of chlorine. When diluted to 0.34*N*, 18,000 gallons of treating solution is obtained. Toward the end of the chlorine absorption, the rate of flow of the chlorine should be reduced, and further addition made under laboratory control of the alkalinity.

If the gasoline, or naphtha, to be treated contains hydrogen sulfide, the gasoline is commonly first washed with sodium hydroxide or other alkaline solution to remove the hydrogen sulfide, as otherwise elemental sulfur is set free from the hydrogen sulfide by the oxidation effect of the hypochlorite. The hypochlorite solution is then applied, and, according to Dunstan,⁷⁹ the gasoline may be finished by further washing with sodium hydroxide solution. Water washing, if found helpful, may be introduced at any place in this treating process. The preliminary sodium hydroxide and water washing are often omitted. If cracked distillates are to be sweetened, preliminary caustic wash is recommended by Dunstan and Brooks and others.^{84, 205, 259} One of the industrial bulletins¹⁶⁹ recommends an initial wash with 3 per cent by volume of 8° to 14° Bé. caustic solution, followed by a water wash. Thus a sodium hydroxide wash may precede or follow the hypochlorite treatment, or one may precede and one follow the treatment.⁷⁹ The partly spent alkali solution from the caustic washing subsequent to the hypochlorite treatment may be utilized for the preliminary caustic washing of succeeding portions, or batches, of naphtha before the hypochlorite treatment.⁸²

The hypochlorite treatment may be applied in two stages. Roughly two-thirds of the total quantity, which is determined experimentally, is used in the first stage, and one-third in the second stage. The nearly spent hypochlorite solution used in the second stage of treatment can be used in the first stage of treatment of a fresh batch of oil to exhaust the solution completely.¹⁸⁷

The naphtha and hypochlorite solution are mixed by any of the known means. Thorough mixing is very important. When agitation by means of a centrifugal pump is used, the mixture is discharged below the surface of the liquid in the settling tank; the aqueous solution is withdrawn at the bottom, and the naphtha at the top.^{42, 84} Various adsorbents, particularly

bauxite, may be used to advantage for improving the color of the naphtha after the hypochlorite treatment.^{79, 84}

The total volume of the hypochlorite solution used in treatment depends on the character of the distillate and, as might be possible in some locations when desulfurization is sought, on the degree of refining desired. For sweetening only, a limited quantity of hypochlorite is required; but for desulfurization, if such is at all practical, a larger volume is used. When sweetening alone is attempted, the consumption of hypochlorite may amount in terms of chlorine to only 2 to 3 pounds per 1000 gallons of a gasoline (0.08 to 0.12 pound per barrel); but for any appreciable desulfurization of the same gasoline, the consumption may be 20 pounds per 1000 gallons in addition to other extensive treatment.⁸⁴ In treating two samples of Mexican oils in two stages with hypochlorite solution by the method of Dunstan and Brooks and then filtering the oils through bauxite, 68 per cent and 40 per cent, respectively, of the total sulfur of the two oils was removed. Of this sulfur, only 25 per cent and 8 per cent of the total amounts in the respective samples was removed directly by hypochlorite, whereas the remainder of the sulfur removed was taken out by means of alkali washes and bauxite.^{251, 260} The two hypochlorite washes were each equal to the oil in volume. The strength of the hypochlorite in both solutions was 0.6*N*. The free caustic soda in the first solution was 0.5 gram per liter; and in the second it was initially between 0.2 and 0.3 gram per liter, but while the solution was agitated with the oil, carbon dioxide was introduced to lower the free alkalinity still further. The actual consumption of hypochlorite was thus 15 pounds per barrel of oil. Dunstan⁸³ describes his process of refining Persian light straight-run oils with hypochlorite solution and testing chemical stability of the oils by mixing 100 cc. of the oil with 1 cc. of 0.1*N* potassium permanganate solution and 2 cc. of sulfuric acid and agitating vigorously; the color did not revert for at least ten minutes. However, the value of this color test is open to question. Dunstan points out that the test is not applicable to cracked gasoline. The copper dish test and the doctor test were both negative. In one of the treating processes, the gasoline which was to meet the above tests was first washed with water, then treated in two stages with hypochlorite solution, washed with caustic, washed with water, and redistilled over sodium hydroxide. By treatment with a hypochlorite solution in the proportion of 1.35 grams of chlorine per liter of oil (approximately one pound per barrel) the sulfur content of one of these oils was reduced from 0.08 to 0.03 per cent; the total cost is given as less than 5 cents per barrel.²²

Natural gasoline is treated similarly to the other grades of gasoline,^{117, 272} an alkali wash being used before the hypochlorite solution if necessary because of hydrogen sulfide.

Treatment with Calcium Hypochlorite

The sweetening of straight-run distillates with calcium hypochlorite solution has proved satisfactory. It is cheaper than sodium hypochlorite, and for small plants it is more convenient to use.

In one of the very early methods of treating with calcium hypochlorite, the oil was treated successively with a suspension of the chloride of lime, sulfuric acid, and sodium plumbite solution, the sodium plumbite being used to remove the chlorine compounds from the oil.¹⁰⁷ Calcium hypochlorite has long been known to be effective for the deodorization of oils because of its ability to destroy the odoriferous mercaptans.

Gaggin¹¹⁴ deodorizes oil with calcium hypochlorite at not over 140° F. and specifies the importance of temperature control. Farrar⁹⁸ deodorizes residuum by heating with chlorine or calcium hypochlorite.

Calcium hypochlorite solution can be prepared by mixing bleaching powder with water, and it is also practical to pass chlorine into an aqueous suspension of lime. The solution made from the lime and chlorine is permitted to settle, and the clear solution of calcium hypochlorite used.²⁸ In the actual treatment of the oils, it is customary to use a calcium hypochlorite solution saturated with lime so as to insure sufficient alkalinity, and for this reason the stock solution is preferably diluted to the proper concentration with water saturated with lime.²² The details of preparing the stock solution are similar to those described in connection with preparing the sodium hypochlorite solution. A solution of hypochlorite made from 2680 pounds of quicklime, 3000 gallons of water, and 2300 pounds of chlorine, yields on dilution 18,000 gallons of 0.34*N* solution suitable for treating. For treating cracked distillates it has been recommended that this solution be diluted with saturated lime solution and then enough sodium hydroxide solution added to produce the desired concentration of hydroxyl ion.

For those desiring to use bleaching powder, high-grade products are recommended, such as an American product under the trade name H.T.H. of the Mathieson Alkali Works, Inc., which is exceptionally stable and has a chlorine content of 65 per cent, whereas normal bleaching powder usually contains only 30-32 per cent.

The treatment of oils with calcium hypochlorite, as with sodium hypochlorite, has been advocated either for sweetening or for sweetening and desulfurization. The degree of desulfurization depends on the constituents of the oil and on the amount of hypochlorite used. However, other methods of desulfurization are almost certain to be more economical.

Calcium hypochlorite treatment, like the sodium hypochlorite, is often combined with other treating processes. The oil may, for example, be treated successively with a solution of calcium hypochlorite, with 98 per

cent sulfuric acid, with 5° Bé. caustic soda solution, and then with water and adsorbents. Brooks and Parker⁴⁷ have patented a process for applying anhydrous aluminum chloride to the sweetened oil for further improvement. Blumenberg³⁴ claims advantages for the use of aluminum sulfate alone with the calcium hypochlorite for removing color and odor from cracked gasoline. The mixture is agitated for 30 minutes and gradually heated to 122 to 140° F., the sludge separated, and the gasoline redistilled. No data are available on the character of the redistilled gasoline from the Blumenberg treatment.

Treatment with Hypochlorous Acid

As mentioned earlier, the treatment of oils with hypochlorous acid, or with a solution of chlorine in water, has not been feasible because of the chlorination of the oil. For this reason, this treatment will be described very briefly, as it is of historical interest only.

Dunstan⁸⁰ treats the oil directly with hypochlorous acid or with a solution of chlorine in water, distills it, and washes it with a weak sodium hydroxide solution. He reports treating a sample of straight-run naphtha containing 0.146 per cent sulfur with 0.426 per cent of chlorine by weight (about 1.2 pounds per barrel), distilling, treating with bauxite or similar adsorbent, or further treating with an anhydrous metallic chloride, such as that of aluminum or zinc, and reducing the sulfur content to about 0.01 per cent.^{80, 81} The behavior here reported doubtless was very exceptional.

Treatment of Hydrocarbons in Vapor Phase with Hypochlorite Solution

The treatment of hydrocarbons in the vapor phase with hypochlorites has not found wide recognition, though some methods for such treatment have been advanced. In one process⁷¹ it is claimed that hydrocarbon distillates from cracking oils can be sweetened and to some extent desulfurized by treatment in the vapor phase with an atomized hypochlorite solution or other alkaline and oxidizing material in a water solution. The solution is sprayed into the vapors at the outlet end of the dephlegmator or fractionating tower, or in a special scrubber. It is also suggested that the hydrocarbons be given a preliminary treatment with sulfuric acid.

Treatment with Chlorine

The use of chlorine in refining petroleum was attempted long ago.²³⁶ It was first recommended for the removal of the objectionable odors of oil, the chlorine being bubbled into the oil, and the excess removed by blowing air through the oil.¹¹³ The desulfurizing effect of chlorine gas on oil was also recognized early in the oil industry.⁴³ Chlorine gas or a solution of the gas in water was applied to the oil. The latter method is described in

this chapter under Treatment with Hypochlorous Acid, since chlorine interacts with water with the formation of hydrochloric and hypochlorous acids.

A higher percentage of sulfur can be removed by treating oil with chlorine at elevated temperatures, from 212 to 250° F. being indicated.¹⁸¹ Walkley and Bargate²⁴⁹ have patented claims for desulfurizing oils by first vaporizing them with steam, introducing chlorine into the vapors, and then condensing the vapors and washing with alkaline solutions. This, of course, is a drastic treatment and could be practical only under very exceptional conditions.

Many by-products can be made by treating hydrocarbons with chlorine; but this phase of the behavior of chemicals on petroleum products will not be discussed here as it does not pertain intimately to the subject of refining.

Koch and Burrell¹⁶⁵ describe the manufacture of amyl acetate from chloro-pentanes. Killeffer¹⁵² describes the manufacture of ethylene dichloride and ethylene glycol. Burgess and Anfigoff⁵¹ produce non-inflammable products from gasoline by subjecting its vapors to the action of chlorine gas and by adding to the product a small quantity of carbon tetrachloride. Blakeman³⁸ treats paraffin wax, naphthalene, etc., with chlorine and uses the resulting products in paints.

Extraction of Mercaptans by Increasing the Solvent Power of Caustic Alkali Solutions

The use of caustic alkali solution for the extraction of mercaptans from the naphthas, or light oils, was discussed in Chapter IV; it was pointed out that only the low molecular weight alkyl mercaptans and the strongly acid aryl mercaptans (thiophenols) could be removed by the alkali solution.

Yabroff and associates^{264, 265, 266, 267, 269} of the Shell Development Company find that the mercaptan-extracting power of the aqueous caustic alkali solution can be enormously augmented by the addition of a substance termed "Solutizer," such as the sodium or potassium salt of a fatty acid having from 3 to 5 carbon atoms. A high degree of solubility of these fatty acid salts in the alkali solutions is desirable; sodium isobutyrate is the most soluble, as illustrated in the second to last column of Table 42.

Table 42. Solubility of Sodium Fatty Acid Salts in 5N Caustic Soda Solution, and Maximum *K* Values for Normal Amyl Mercaptan in the Solutions.

Salt	Number of Carbon Atoms in Salt	Solubility of Salt in 5N NaOH Solution (grams/100 cc.)	<i>K</i> for <i>n</i> -Amyl Mercaptan
None	0	..	1.0
Sodium acetate	2	20	1.3
Sodium propionate	3	30	15.5
Sodium <i>n</i> -butyrate	4	28	16
Sodium isobutyrate	4	45	140
Potassium isobutyrate	4	50	210
Sodium <i>n</i> -valerate	5	14	8
Sodium trimethyl acetate	5	12	8.5
Sodium caproate	6	6.7	4.5

In the last column of Table 42 are given the partition coefficients, K , for normal amyl mercaptan between the alkali solution and the hydrocarbon solution. The factor K is the quotient of the concentration of the mercaptans in the alkali solution divided by the concentration of the mercaptans in the hydrocarbon liquid. Table 42 indicates that if a naphtha-amyl mercaptan solution is agitated with an equal volume of a 5*N* caustic soda solution (about 20 per cent caustic) the mercaptan will be equally divided between the naphtha and the alkali solutions ($K = 1$); but if the naphtha-mercaptan solution is agitated with an equal volume of the caustic soda solution saturated with sodium isobutyrate (45 grams isobutyrate per 100 cc. of caustic solution), the quantity of mercaptan in the alkali solution will be 140 times greater than in the naphtha solution ($K = 140$). The sixth line of data of the same table show the greater influence of potassium salt over the sodium salt in promoting the extraction of mercaptans; for the same concentration, it is about 50 per cent greater.

The combined influence of the caustic alkali and alkali salt in comparison with each separately is illustrated in Table 43.

Table 43. Combined Effect of Caustic Alkali and Alkali Isobutyrate in Extracting *n*-Amyl Mercaptan from Naphtha.

Solution in Water	K Value at 68° F.	% Mercaptan Extracted with 10% by Volume Aqueous Solution
3.09 <i>N</i> Potassium Isobutyrate	0.0005	0.01
6 <i>N</i> KOH	1.36	11.97
3.09 <i>N</i> Potassium Isobutyrate + 6 <i>N</i> KOH	384.0	97.4

The solubility of the alkali salts of the fatty acids having more than 5 carbon atoms in caustic alkali solution is too low for the most practical use, although at their necessarily low concentration they exert greater influence than an equal weight of the sodium isobutyrate.

The desirable composition of the solutizer solutions²⁶⁶ is from 3 to 6*N* alkali hydroxide together with about 3*N* isobutyrate salt. A greater concentration of the caustic soda does not increase the mercaptan removal because of its salting out effect.*

Yabroff points out²⁶⁴ that the efficiency of the solutizer process depends on the increase in solubility of the unneutralized mercaptans in the alkaline solution and on the consequent increase in the total amount of mercaptans dissolved in the alkali as mercaptides. The difference in the acidities of the different alkyl mercaptans is far too little to affect materially their extractibility in aqueous caustic alkalies alone, but the large alkyl groups of the larger mercaptan molecules increase the solubility of such mercaptans in

* Methyl alcohol has a marked solutizer effect on aqueous caustic soda for extracting mercaptans.²⁶⁸

the oil phase and militate against their extraction by any process. A decrease in the temperature increases the extractibility of the mercaptans, but the nature, or composition, of the naphtha has very little effect.

Because the solutizer process actually extracts sulfur from the naphtha or gasoline, the treated gasoline has greater lead susceptibility than unsweetened gasoline or gasoline sweetened by converting the mercaptans into disulfides.^{266, 267}

The mercaptans are extracted from the sour naphtha in a countercurrent manner. The spent alkaline solution is regenerated by stripping it with steam; it is re-used to sweeten further quantities of naphtha. Yabroff, White, and Caselli²⁶⁹ have described the regeneration process, theories involved, steam consumed, etc.

The development of this process is new; at the time of publication of this book, the process had been tested in commercial operations and found capable of completely sweetening naphthas of normal end boiling points. The process may remove too completely the natural inhibitors, the alkyl phenols, from the naphtha and increase the autoxidation of the gasoline; but this condition is remedied by re-adding some of the extracted phenols to the naphtha.

Treatment with Alcoholic Solutions of Alkalies and Alkali Metals

The treatment of oils with small quantities of alcoholic alkali solutions may have as its purpose either stabilization of the color,¹⁸⁰ or total or partial sweetening and the correction of corrosiveness. Aqueous methanol-alkali solution has been patented by the Atlantic Refining Company, and licensed by the Universal Oil Products Company, for extracting mercaptans from gasoline.^{99a} Alcoholic solutions of sodium and potassium hydroxides, which can be prepared by dissolving the corresponding dry hydroxides in anhydrous or nearly anhydrous alcohol, act with oxygen or air as feeble sweetening agents. The presence of more than 3 to 5 per cent of water in the alcohol impairs the quality of the reagent.

Elemental sulfur is slowly absorbed (in several hours) from gasoline by alcoholic caustic soda solution, and the gasoline made non-corrosive. The elemental sulfur is, however, much more readily removed by alcoholic potash solution than by alcoholic caustic soda solution. A simple method of applying this reagent on a commercial scale is to mix about 0.1 to 0.2 per cent by volume of it with the oil with good agitation, and to let the mixture stand. The amount required depends on the quantity of elemental sulfur in the gasoline.

Vesselovsky and Kalichevsky²⁴⁷ have reported their investigation on removing mercaptans and elemental sulfur from gasoline. For the removal of mercaptans, they show that alcoholic solutions of sodium hydroxide are

much more active than alcoholic potash solutions, whereas for the removal of elemental sulfur, the opposite is true. An anhydrous ethyl alcoholic solution of potassium hydroxide (21.8 per cent potash solution), when contacted with the gasoline, brings about a reaction between one atom of the elemental sulfur per molecule of potassium hydroxide in about two minutes, and of about 1.3 atoms of sulfur per molecule of the alkali in 5 to 10 minutes, even though more sulfur is available for absorption. Table 44 is from the report and shows in more detail the rates of absorption of sulfur by alcoholic potash. Samples of the gasoline were taken and examined after the intervals of time indicated.

The second half of the table, in which less agitation occurred than in the first, indicates that the alkali separates from the naphtha after the one-minute agitation so that later the contact between elemental sulfur and alkali is greatly diminished, a factor which doubtless accounts for the lower absorption of the sulfur in the work represented by the table.

Table 44. Effect of Time in Treating a Solution of Elemental Sulfur in Naphtha with a Deficient Quantity of Potassium Hydroxide Dissolved in Absolute Ethyl Alcohol.

KOH in Naphtha (gm./liter)	Sulfur in Naphtha (gm./liter)	Time of Contact (min.)	Sulfur in Solution (%)	Mol-Ratio of Sulfur Removed to KOH Added
<i>One-minute agitation at beginning of treat followed by moderate occasional shaking of reacting mixture.</i>				
1.240	1.779	0	0.251	...
		5	0.145	1.18
(Mol-Ratio of KOH and S added = 1 : 2.5)		10	0.133	1.32
		15	0.132	1.33
		30	0.130	1.35
		60	0.112	1.55
		120	0.062	2.11
		1440	0.080	1.91
		2880	0.138	1.26
<i>One-minute agitation at beginning of treat only.</i>				
1.532	1.975	0	0.339	...
		2	0.199	1.00
(Mol-Ratio of KOH and S added = 1 : 2.25)		3	0.176	1.17
		5	0.161	1.29
		10	0.161	1.29
		15	0.166	1.24
		30	0.167	1.23
		60	0.165	1.25
		129	0.166	1.24
		930	0.157	1.30
		2880	0.165	1.25
		5900	0.179	1.14

When a lower ratio of sulfur to alkali was used in different experiments, the sulfur was completely removed. The following two experiments are presented as illustrations of the amount of sulfur that can be removed com-

pletely enough to render gasoline non-corrosive. In one experiment, 6 cc. of 21.8 per cent solution of potassium hydroxide in ethyl alcohol, by weight, was agitated with 200 cc. of a 0.227 per cent solution of elemental sulfur in gasoline. The gasoline was made non-corrosive to the copper strip and would not even give a positive reaction for sulfur in the very sensitive ethyl mercaptan-plumbite solution test. In the second experiment, only 4 cc. of the alcoholic potash solution was added to 200 cc. of the sulfur-gasoline solution; but after the agitation, enough sulfur remained in the gasoline to give a slight positive reaction in the ethyl mercaptan-plumbite test, although not enough remained to render the gasoline corrosive to the copper strip. In this second experiment, approximately one molecule of potassium hydroxide was used per atom of sulfur. The presence of water diminishes the desulfurizing power of alcoholic potash.

The chemistry of the reaction between elemental sulfur and alcoholic solutions of alkalis is complex. Some metallic sulfides, polysulfides, and thiosulfates are formed, and it is possible that the reaction proceeds in the same general manner as that of sulfur and potassium carbonate in an alcoholic solution.⁶⁸

Alcoholic solutions of the metals sodium and potassium react with mercaptans and with elemental sulfur in the gasolines in about the same manner as their hydroxides.

Aluminum alcoholate can also be used to remove elemental sulfur from gasoline, though no advantages exist over the treatment with the alkali hydroxide solutions, especially alcoholic potash. Moreover, the preparation of the aluminum alcoholate is more difficult.⁵⁶

THE REDUCTION OF TOTAL SULFUR IN LIGHT PETROLEUM DISTILLATES

Almost all kerosenes and gasolines are refined so that the total sulfur content in the finished product is reduced to some given percentage below which the cost of treatment is not justified by the improvement in the quality. The sulfur in kerosene burns to sulfur dioxide, which is detrimental to long and satisfactory burning of the kerosene, as shown in Chapter II. Sulfur in gasoline is objectionable because it degrades its octane rating and especially its tetraethyl lead susceptibility. Observations and investigations show that though the sulfur dioxide formed in the combustion of the fuel may not be especially injurious to the modern automobile, nevertheless if it leaks by the piston rings and dissolves in the lubricating oil with moisture present, it may become a corrosive acid and attack the metal surfaces lubricated by the oil. This effect of the sulfur dioxide is negligible when the lubricant is kept warm, as the heat expels both the moisture and the sulfur dioxide; it is particularly active only in cold weather and when the engine is idle.⁷³ Combined sulfur in the lubricating oil is not a factor

in this corrosiveness except in the almost negligible portion actually burned in the cylinder.

The maximum content of 0.1 per cent sulfur sometimes specified for motor fuels is now considered more drastic than necessary to protect modern automobiles from corrosion, and also too drastic if evaluated on the cost of eradication of the sulfur and on the octane values, if tetraethyl lead is not to be added. However, if tetraethyl lead is to be added, it may be economical to reduce the sulfur much lower than to 0.1 per cent, even to 0.02 per cent, for sulfur greatly lowers the susceptibility of gasoline to lead. The influence of sulfur on tetraethyl lead has given a very marked economic impetus to further advances in desulfurization.

Komski¹⁰⁰ reports that, in the absence of mercaptans, 0.15 per cent sulfur has no corrosive effect in a motor, and in mild weather as much as 0.4 per cent is allowable. In cold weather, however, the sulfur content should be below 0.2 per cent to prevent corrosion. Sulfur has very little effect on the octane rating of unleaded gasoline; the octane rating of this gasoline is lowered only about three points by 0.4 per cent sulfur. However, if tetraethyl lead is used, 0.4 per cent of sulfur in the gasoline may lower the octane number 15 points. For the highest efficiency of tetraethyl lead, the sulfur in gasoline must not exceed 0.02 per cent. (*See also* page 33.)

The accepted figure for the percentage of sulfur in kerosene is not uniform, but usually is about 0.1 per cent. Kerosene stock refined with sulfuric acid or sulfur dioxide, or a combination of the two, to give good color and satisfactory burning quality usually meets the sulfur requirements.

The poor burning qualities of kerosene, manifested in a smoky flame and carbonization of the lamp wick, instability of color, etc., are usually due to hydrocarbon constituents having a high carbon-to-hydrogen ratio and a high specific gravity, such as the aromatic compounds; as yet no method has been developed for producing a good kerosene from a stock containing such compounds without first eliminating them. A treatment removing only the sulfur compounds from such a kerosene stock would not be of practical importance.

Different criteria exist for the refinement of gasoline from those for kerosene. From gasoline the elimination is desired only of the sulfur compounds and other chemically active compounds which become colored, form gums, and undergo changes which intensify the detonation. Because of these criteria, the Edeleanu process is not suitable for gasoline, since it removes the desirable aromatic compounds along with the sulfur compounds. Exceptional stocks, however, may contain large amounts of acidic sulfur compounds, such as hydrogen sulfide and low molecular weight mercaptans, which can be removed by washing with strong alkali solutions; but as yet the only method that has come into extensive use for desulfurizing gasoline, straight-run or cracked, is that of strong sulfuric acid under carefully controlled conditions, as described in Chapter II. With

the use of acid the loss of the aromatic compounds is far less than with the liquid sulfur dioxide. Cracked gasoline with few, if any, exceptions contains much more sulfur than the straight-run gasoline produced from the same crude oil; in some sections of the country the cracked product requires from 10 to 50 pounds of acid per barrel to reduce the sulfur content to 0.1 or to 0.15 per cent, and the cost of such refining may run from \$0.25 to \$0.75 per barrel.

Because of the importance of the subject of sulfur reduction in motor fuels, many investigations have been undertaken on methods for reducing the sulfur, but at present none has been found comparable to the use of sulfuric acid. It is possible that the beginning of the proper solution is in the present trend in manufacturing non-detonating gasoline by the cracking and reforming operations with the use of catalysts, which eliminate much of the combined sulfur as hydrogen sulfide, or otherwise.

A brief review of the types of these experiments on sulfur reduction will serve as a supplement to the preceding discussions of acid treatment, sweetening, and perhaps solvents, in which the subject of sulfur removal has necessarily been considered. No extensive tabulations of the results of the experiments have been attempted.

Types of Sulfur in Light Oils

The nature of the sulfur compounds in petroleum products was noted earlier in this chapter (Table 31, page 179). Usually the greater percentage of sulfur occurs in the form of the chemically stable and inert thiophenic compounds, although the previous history of the oil necessarily introduces many exceptions. If, for example, a crude petroleum containing elemental sulfur in solution is heated, the sulfur reacts with the oil and forms hydrogen sulfide and complex sulfur compounds; if the oil is heated to cracking temperatures, the hydrogen sulfide released may combine with newly-formed olefins to yield mercaptans; the mercaptans may react with olefins to yield sulfides, etc.¹⁴⁷ In the usual thermal cracking operations some of the normally stable thiophenic (ring) sulfur compounds are cracked into smaller thiophenic molecules that distill with the gasoline.

Table 45 contains the percentages of sulfur in the different sulfur com-

Table 45. Chemical State of Sulfur in Untreated Cracked Gasolines.
(Per Cent Sulfur by Weight.)

Sulfur	California Midway	Smackover	Surachany (Russian)
Elemental	none	none	0.005
Hydrogen sulfide	present	present	present
Mercaptan	0.02	0.02	0.004
Disulfide	0.11	0.03	0.006
Sulfide	0.02	0.00	0.003
Thiophene (residual)	0.95	0.15	0.038

pounds in two samples of American cracked gasoline⁹⁷ and one Russian cracked gasoline.⁷⁶

The data of Table 46, developed by Sachanen,²¹² show the content of sulfur in the different crude oils and that of the straight-run and cracked gasoline produced from the crude oils.

Table 46. Sulfur Content in Crude Oils and in the Straight-Run and Cracked Gasolines Produced from the Crude Oils.

Crude Stock	Crude	Straight-Run Gasoline	Cracked Gasoline (Untreated)
Pennsylvania	0.04	0.005	0.02
Oklahoma City	0.2	0.01	0.04
Seminole	0.4	0.015	0.015
East Texas	0.3	0.01	0.012
West Texas	0.8	0.12	0.12
Texas Panhandle	0.5	0.055	0.21
Gulf Coast, Placedo	0.15	0.02	0.08
California, Huntington Beach	1.3	0.17	0.8
California, Santa Fe Springs	0.4	0.05	0.2
Smackover	2.0	0.04	0.19
Mexico, Panuco	5.2	0.06	1.4
Mexico, Posa Rica	1.8	0.05	0.8
Venezuela, La Rosa	1.8	0.07	0.7
Russia, Grozny	0.2	0.015	0.018
Russia, Surachany	0.3	0.017	0.066
Iran	0.8	0.08	0.16
Iraq	2.0	0.1	0.34

The percentage of sulfur in the gasolines is dependent on the percentage of sulfur in the crude oil but obviously is not directly proportional to it. The percentage of sulfur in the cracked gasoline is much greater than in the straight-run gasoline from the same crude oil.

McKittrick¹⁰⁴ found that nearly all the sulfur compounds in a sample of California cracked gasoline containing 1.0 per cent combined sulfur were members of the thiophene series; he identified such compounds as methyl thiophene, ethyl thiophene, dimethyl thiophene, etc.

Desulfurizing with Aluminum Chloride

Anhydrous aluminum chloride has been used not only as a catalyst for pyrolysis, or cracking, but also for desulfurizing, decolorizing, deodorizing, and increasing the saturation of unsaturated distillates.

Ferrous and ferric chloride, mixtures of aluminum and calcium or mercuric chloride,¹⁰⁴ and finely divided metals in the presence of chlorine¹⁰³ act similarly to aluminum chloride but are less effective. A bibliography relating to the action of aluminum chloride on hydrocarbons, dating from 1886, is given by Berl and Lind.²⁰

The use of aluminum chloride for the treating and cracking of oils has long been known,¹¹⁰ but its cost of from four to five cents per pound is still too high for extensive use. The chemistry of aluminum chloride treat-

ment is complicated, and no explanation of the details is attempted here. When an oil is treated with this reagent, some of the unsaturated hydrocarbons are polymerized¹⁹⁵ or condensed with other compounds, and other hydrocarbons are split, or cracked, into lighter substances. Youtz and Perkins²⁷¹ investigated the activity of aluminum chloride in removing several pure representative organic sulfur compounds from straight-run cleaners' naphtha. They refluxed 100 cc. of the naphtha, to which was added the sulfur compound, with 1 gram of aluminum chloride (equivalent to 3½ pounds per barrel) at 210 to 212° F. for 3 to 4 hours, decanted half of the naphtha, and distilled the remainder from the aluminum chloride. The decanted and the distilled portions were both washed and dried, and their contents of sulfur determined. The results on the sulfur reduction are shown in Table 47.

Table 47. Effect of Aluminum Chloride Treatment on Sulfur Content.

Compound	Original Solution Per Cent	After Refluxing Per Cent	After Distilling Per Cent
Ethyl sulfide	0.477	0.448	0.373
Isoamyl sulfide	0.511	0.380	0.170
<i>n</i> -Heptyl sulfide	0.445	0.324	0.312
<i>n</i> -sec-Heptyl sulfide	0.446	0.019	0.032
Allyl sulfide	0.624	0.056	0.027
Phenyl sulfide	0.507	0.377	0.052
Benzyl sulfide	0.400	0.012	0.000
Ethyl disulfide	0.573	0.422	0.226
Isoamyl disulfide	0.460	0.330	0.122
	0.479	0.294	0.180
Trimethylthiophene	0.537	0.365	0.236
Trimethylethylthiophene	0.410	0.231	0.100

All the compounds examined were affected by this method of treatment except the ethyl and *n*-heptyl sulfides. The disulfides were for the most part reduced to mercaptans.

Stransky and Hansing and others²⁸³ have recommended a temperature of 95 to 150° F. for the refining of light petroleum distillates with the aluminum chloride.

Downs has patented methods for filtering the heated distillate through a filter bed containing aluminum chloride⁷⁴ or for condensing the distillate in the presence of the aluminum chloride.⁷⁴

Preliminary refining with sulfur dioxide by the Edeleanu process has been patented for special use in facilitating subsequent treatment with aluminum chloride;^{3, 123} and because of special selectivity of the liquid sulfur dioxide for sulfur compounds, its use on any distillate to be charged to a cracking plant is worthy of consideration whenever a gasoline of particularly low sulfur is demanded.

The desulfurization of cracked gasoline by means of aluminum chloride

is accompanied by a large loss of the unsaturated constituents and a large consumption of the reagent itself. Its use, therefore, is uneconomical for such purposes.

Aluminum chloride acts as a polymerizing and saturating agent. It can be used for producing lubricating, transformer, medicinal, and other similar oils.⁴⁸ It is of interest to note that any given oil seems to be capable of being saturated to a certain degree by the aluminum chloride treatment, but that further amounts of the reagent do not increase this degree of saturation.

Activated Aluminum for the Removal of Elemental Sulfur

Granular or finely divided aluminum which is activated by mercuric chloride solution in alcohol, or otherwise, can be used to remove elemental sulfur from gasoline and to render gasoline non-corrosive. As aluminum is a comparatively strong reducing agent and reduces disulfides to mercaptans, it cannot be used for treating gasolines which contain disulfides. Some improvement in the color of the oil also results from the treatment with activated aluminum.

Catalytic Desulfurization. Houdry Process

The trends in desulfurization of motor fuels are toward the use of catalysts, especially during cracking.

The results of desulfurizing by the Houdry catalytic refining process (not cracking process) are briefly described in the chapter on Adsorbents (page 298), and the desulfurizing effect of the Houdry catalytic cracking process has been described in the literature.¹⁴² Several of the Houdry catalytic cracking plants and at least one catalytic refining unit have been installed. All the details of the operations of these units will doubtless be published in the near future. In both processes (the refining and the cracking) hydrosilicate of aluminum (an adsorbent earth material) with or without the addition of certain metals is used as catalyst. The catalyst soon loses its activity but is immediately regenerated *in situ*. Two catalyst chambers are used, one on stream, and the other in the regeneration stage.

The data of Table 48 are taken from a report on the Houdry catalytic cracking of different types of gas oil. Attention is called to the sulfur reduction figures.

The Perco Desulfurization Process of the Phillips Petroleum Company of Oklahoma

The Perco process is not a cracking process but is essentially a vapor-phase desulfurizing process for the lighter oils. The vapors are passed through bauxite as catalyst at about 700 to 750° F. The process has been

described by Schulze and Alden and by others.²¹⁷ They point out that the very light gasolines and the natural gasolines having very little cyclic sulfur compounds can be thus rendered almost sulfur-free; the sulfur of the sulfur compounds, such as mercaptans, monosulfides, and disulfides, is converted into hydrogen sulfide, which can be removed by an alkali wash. As

Table 48. Houdry Catalytic Cracking. Yield and Product Characteristics by Running Gas Oils One Pass.

Type Crude	Mid-Continent Gas Oil	West Texas— New Mexico Gas Oil	East Texas Gas Oil	Coastal Gas Oil
Sulfur content of charge to plant (%)	0.22	0.81	0.16	0.04
Charge to catalyst:				
A.P.I. gravity, deg.	37.8	30.4	34.5	30.0
Initial boiling point (°F.)	416	440	420	406
50-per cent point (°F.)	536	554	574	494
End point (°F.)	656	683	750	602
Dry gas, % by weight of charge to catalyst	4.3	5.2	6.1	4.9
Catalyst deposit, % by weight of charge to catalyst	3.3	4.0	3.2	1.0
Gasoline:				
% by volume of charge to catalyst	4.47	41.0	44.4	50.3
A.P.I. gravity, deg.	64.4	60.8	62.7	56.8
50-per cent point (°F.)	233	230	242	260
90-per cent point (°F.)	346	354	362	382
End point (°F.)	398	404	402	410
Sulfur content (%)	0.02	0.07	0.02	0.01
Copper-dish gum, mg. per 100 ml.	3	9	4	4
Octane No., A.S.T.M. Motor Method	79.2	79.3	77.0	80.8
Catalytic gas oil:				
% by volume of charge to catalyst	53.0	55.3	51.9	49.9
A.P.I. gravity, deg.	35.2	27.4	31.0	26.6
Initial boiling point (°F.)	409	419	468	414
50-per cent point (°F.)	510	516	550	480
Pour point (°F.)	+5	-(-60)	+15	-(-60)
Viscosity (Saybolt Universal) at 100° F. (sec.)	36	37	36	34
Sulfur content (%)	0.07	0.8	0.1	0.1
Aniline point (°F.)	148	116	142	74
Liquid recovery, per cent by volume of charge to catalyst	97.7	96.3	96.3	100.2
32°-A.P.I.-gravity furnace oil in catalytic gas oil (%)	100	40.2	90	

an example, a Borger, Texas, natural gasoline, suitable for aviation gasoline blending and having the 90 per cent A. S. T. M. distillation point at 201° F., Reid vapor pressure of 12 pounds, and sulfur content of 0.037 per cent, was in three experiments desulfurized to different degrees, and on each desulfurized product the octane number and the response to tetraethyl lead were determined, as shown in Table 49.

Table 49. Octane Number and Average TEL Requirements of Borger 12-Pound Natural Gasoline.

% Sulfur Average Octane No., A.S.T.M.:	Undesulfurized	Desulfurized		
	0.037	0.008	0.004	0.002
Initial	67.2	69.5	69.6	69.7
+ ½ cc. TEL	72.2	76.5	76.8	77.0
+ 1 cc. TEL	75.6	80.0	81.0	81.4
+ 2 cc. TEL	79.6	82.0	84.3	84.9
+ 3 cc. TEL	82.1	85.3	86.8	87.5
+ 4 cc. TEL	84.0	87.6	89.2	89.7
+ 6 cc. TEL	86.6	91.2	92.8	93.2
TEL Saving to 76-Octane No. (%)		58	60	62
TEL Saving to 82-Octane No. (%)		46	57	62
TEL Saving to 88-Octane No. (%)		43	52	56

Attention is called to the great increases in the lead susceptibility of the natural gasoline as the sulfur is reduced progressively to almost zero.

The general trends in the catalytic cracking refining of oils are reviewed by Foster¹⁰³ and by Van Voorhis.²⁴⁵

Desulfurizing with Hypochlorite

The use of hypochlorite solution for sweetening of straight-run or other chemically stable hydrocarbons was discussed earlier in this chapter. It was noted that unless the reagent was kept alkaline, it could not be applied to cracked naphthas because of the tendency to chlorinate the olefins and other reactive hydrocarbons; and the chlorinated products were more detrimental to a motor than the mercaptan sulfur.

Hypochlorite has been considered as a desulfurizing agent for uncracked stocks. Bolko, Englin, and Chuvikova³⁶ experimented with desulfurizing a gasoline containing 0.49 to 0.58 per cent sulfur by means of hypochlorite solution made weakly acid. The gasoline, mixed with about 25 per cent by volume of a dilute aqueous sodium hypochlorite solution (containing 15 grams active chlorine per liter), was gradually acidified with small increments of sulfuric acid, and the treated gasoline then contained 0.105 per cent sulfur and 0.13 per cent chlorine. When the gasoline was then distilled over alkali, the chlorine content was reduced to 0.01 per cent or slightly less, and the sulfur to less than 0.02 per cent. If the treated gasoline is heated in an alkali solution under two atmospheres' pressure, the chlorine and sulfur are reduced to practically zero.

A somewhat similar series of experiments has been conducted by Ardagh, Bowman, and Weatherburn.¹¹

Treatment with Metallic Zinc

Finely divided zinc and certain other metals, including copper, iron, lead, manganese, antimony, and their compounds, are claimed by Cross^{64, 65} to remove sulfur when gasoline vapors are passed through them.

Some of the sulfur compounds are claimed to be removed from oil, and the color and stability, especially of cracked distillates, improved by treatment with nascent hydrogen released from zinc in alkali or acid solution.^{123, 214}

Treatment with Mercuric Salts

Mercuric chloride in water or in alcohol solution is used in laboratory investigations for the separation of organic sulfur compounds from oil. Mercaptans and sulfides are more or less completely removed. Borgstrom³⁷ finds that, for the complete removal of mercaptans from light distillates, a solution of mercuric acetate is the most efficient of all the heavy metal salts. His investigation includes tests on 14 different mercaptans. It would not, however, affect all other types of sulfur compounds. According to Engler,¹²³ a saturated aqueous solution of mercuric acetate removes a high percentage of olefinic hydrocarbons from petroleum distillates. The soluble salts of mercury form double salts with organic sulfides, which are insoluble in light petroleum oils. Ramage²⁰¹ removes diolefins by treating cracked distillates with alcoholic mercuric chloride solution.

Treatment with Metallic Mercury

Metallic mercury is suitable for removing all traces of elemental sulfur from oils.¹⁵⁹ It has been shown in the discussion on treatment with sodium plumbite solution for sweetening that metallic mercury may be used advantageously for determining the presence of sulfur in gasoline. It is especially valuable in the laboratory for removing all traces of elemental sulfur from gasoline which is to be used for experimental purposes. It does not combine or react with the mercaptans. Because of the high cost of mercury, it is not suitable for large-scale operations.

Treatment with Metallic Sodium

At 650 to 850° F. the total sulfur content of petroleum distillates can be removed in only a few seconds of contact with a large excess of metallic sodium. Laboratory experiments can be conducted by bubbling petroleum vapors through molten sodium contained in iron apparatus, or by enclosing the whole in a small bomb, heating it externally, and agitating it by rotation or otherwise.

The metal sodium has seldom, if ever, been used in commercial practice because of the high cost, fire hazard, and loss of oil through decomposition. When heated, metallic sodium not only reacts with sulfur and with unsaturated hydrocarbons (olefins) but most probably with certain highly substituted or branched saturated hydrocarbons.⁶³

Metallic sodium has long been used in analytical methods in organic

chemistry for the identification of sulfur, a relatively high temperature usually being imperative, such as the temperature of fusion of non-volatile materials or of heating volatile materials in a pressure bomb or autoclave. Because of this property, sodium has frequently been considered suitable for use in the refining of petroleum, as shown in the following brief extracts of patents.

Under different conditions it has been proposed to apply the sodium as a solid, a molten liquid, or an alloy with some other substance, such as lead, mercury, or ammonia.⁶⁹ Watson²⁵³ has devised different types of apparatus for treating oils with molten metals. The use of metallic sodium in contact with oil during hydrogenation operations at comparatively high temperatures has been patented as a desulfurizing process.¹³⁹ It has been suggested that the treatment with the sodium precede the hydrogenation process.⁹⁹

Treatment with Ferric Chloride

Ferric chloride has been studied as a refining agent for petroleum distillates. Apparently it cannot compete with the better established methods, such as the various modifications of the acid treatment. The behavior of ferric chloride is similar to that of aluminum chloride, but the ferric chloride is less reactive. The following illustrations show its suggested uses.

Goffart¹¹⁶ recommends refining oil by treating it with ferric chloride which is made strongly acid with hydrochloric acid, the mixture being contacted for 10 to 15 minutes. No report is made as to whether the oil becomes chlorinated.

According to another patent,¹⁴⁴ the more unstable constituents are removed from a cracked distillate by heating it with about 2 per cent of crystalline ferric chloride, subsequently distilling the oil and washing with dilute alkali.

Treatment with Ferric Oxide

For the removal of sulfur compounds from petroleum distillates by means of ferric oxide, the vapor-phase process is recommended. The use of ferric oxide in combination with cupric oxide is described under the subject of copper oxide. In one of the old processes the hydrocarbon vapors were passed through a mixture of charcoal and oxides of iron, hydrogen sulfide being the only sulfur compound removed to any appreciable degree.¹⁸⁸ A later refinement by Hood¹⁴¹ of the older development utilizes ignited magnesite, alumina, or bauxite, brought first into contact with the oil vapors to dissociate the sulfur compounds into hydrogen sulfide, the latter being absorbed by the ferric oxide. Another process by Ihrig¹⁴⁰ uses hydrated lime (25 per cent) and iron oxide (75 per cent) to remove the corrosive constituents from the oil. Ferric oxide suspended in water is also recom-

mended for the removal of hydrogen sulfide from gases. The gases are bubbled through the suspension or otherwise contacted with it.⁹⁵ Burwell and Sherman⁵² desulfurize oil in the vapor phase by passing the vapors over an anhydrous mixture of oxides of iron and of an alkali-earth metal.

Postovskii and Plyusnin¹⁹⁸ subjected a crude oil to fractionation, collected the first fraction having an end boiling point of about 520° F., and passed it in the vapor phase with steam through a layer of natural iron ore (iron oxide), maintained at 660 to 840° F. The sulfur was reduced from 1.25 per cent to 0.25 per cent, and a subsequent treatment with about 10 pounds of strong sulfuric acid further lowered the sulfur to 0.14 per cent. The 1.25 per cent of sulfur in the distillate was made up primarily of cyclic (thiophenic) sulfur compounds, but some mercaptans were also present. The loss of oil from decomposition by the iron oxide was 5 per cent, but in a short time the resulting carbon and coke from the oil permeated the ore and lowered its efficiency. It might, however, be possible to revivify the iron oxide.

Retailiau²⁰⁰ and Wyman contact straight-run gasoline in the vapor phase at about 550° F. with a mass of finely divided iron oxide to remove sulfur compounds and to transform them into compounds more soluble in sulfuric acid so as to increase the lead susceptibility.

Blagodarov⁸² desulfurizes gasoline by passing the vapors through a tower of pyrite dross, consisting chiefly of iron and copper oxides. The spent packing is regenerated by superheated steam at 750° F.

Treatment with Metallic Iron

A process has been patented by Claussen and Cobbett⁵⁷ for the successive treatment of oils with finely divided metallic, or "spongy," iron or lead, sulfuric acid, and lime, and redistilling for the removal of the organic sulfur compounds. The process has not been able to compete in cost and efficiency with the more or less standard treatment with sulfuric acid, especially at reduced temperatures.

Lindsay and Davidson¹⁶⁰ blow finely divided iron into hot oil vapors before the vapors reach the condensers. Kotzebue and Bowman¹⁵⁷ and, later, Becker¹⁴ patented processes for purifying oil by passing the vapors through mats of steel wool. Perkins¹⁰² has a similar process, using metallic packing.

Treatment with Cupric Oxide

Some years ago Frasch created much interest in the use of copper oxide in the deodorization of Ohio and Canadian crude petroleum oils. These oils had been for many years practically unmarketable, even as fuel. Frasch developed the general information that the odoriferous constituents

of these crude oils were mainly sulfur compounds which reacted somewhat readily with the oxides of certain metals, especially the oxide of copper. From this information he initiated deodorizing methods, considered at that time very economical, which changed the market value of the crude oil from around 14 cents per barrel to over \$2.00 per barrel. From information later developed, it appears that the odors were doubtless due to sulfur constituents of the type of mercaptans and possibly alkyl sulfides, for the elimination of which from the distillates of today the general processes described under Sweetening serve more economically.¹⁰⁵ The Frasch processes are described in the literature.^{13, 191}

Other descriptions of the use of copper oxide are submitted below, as well as many more recent modifications, which are intended to meet present requirements.

Perkin,¹⁹¹ in reviewing the earliest attempts at actual desulfurization with cupric oxide, says that it was not then found successful because of the large excess required, even to prevent corrosion of stills; but later it was found that certain crude oils were amenable to treatment with the copper oxide, and others were not. Some oils are easily desulfurized, especially in the vapor phase;¹¹⁵ but others, such as those of Mexico or California, under the same treatment are only slightly affected. However, cupric oxide improves the odor and "sweetens" all oils so that they will pass the doctor test, the efficiency of the reagent on a given oil being proportional to the porosity of the copper oxide and the amount of its surface exposed.¹³⁴ The sweetening process can be handled by heating the oil and oxide together and filtering or by distilling the oil from contact with the oxide of copper and of other metals.¹⁰⁵

It is claimed by Frasch, the inventor, that lead oxide serves to remove the sulfur compounds from the lower-boiling constituents of the oil at relatively low temperatures, but cupric oxide is more effective for the higher-boiling constituents, especially at higher temperatures. He recommends for certain oils the use of oxides of lead and iron with the oxide of copper.¹⁰⁶

Inert material has been used with the metallic oxides to increase their surface. For example, a still is charged with 300 barrels of crude kerosene mixed with 15 per cent of heavy residuum, 1600 pounds of litharge, 3000 pounds of cupric oxide, and 3000 pounds of plaster of Paris, the solid constituents being finely divided and kept in suspension in the oil by steam, air, or mechanical agitation, and the oil later distilled from the mixture.²⁰⁴ A typical mixture of materials used consists of 75 per cent cupric oxide, 10 per cent litharge, and 15 per cent ferric oxide.¹⁹¹ Frasch uses the same reagents when treating the oil in the vapor phase as in the liquid phase.¹⁰⁸

In a modified method some of the sulfur and other reactive constituents are removed by filtering the oil while hot through bauxite which has been

impregnated with a solution of copper acetate or other organic salt of copper, and ignited to deposit the copper oxide, or copper. Only about one per cent of copper is used in the bauxite mixture. Direct mixing of bauxite with cupric oxide, cuprous oxide, or copper is said to be equally satisfactory.²⁰⁷

For sulfur reduction, Parsons and Coleman¹⁸⁹ have patented the operation for treating crude oil or its fractions with 1 to 10 per cent of cupric oxide or other mineral oxides having oxidizing properties at a temperature a little below the boiling point of the oil. The material is then introduced into a still containing sodium hydroxide, and the oil distilled.

The metallic sulfides produced from the metallic oxides can be reconverted to the oxides by roasting and also, according to Rather and Shepard,^{6, 203} by the use of superheated steam without roasting.

Treatment with Copper Chloride

Walker²⁴⁸ and Herthel¹³⁶ patented processes for desulfurizing certain oils by passing the vapors over anhydrous cupric chloride and into an alkaline solution of a lead salt. Doubtless there would be danger of halogenating the oil by this method. Copper chloride and other metallic halides are active halogenation catalysts and have been used by Tizard and co-workers²⁴⁰ for the halogenation of methane and other hydrocarbons, a temperature of 930° F. or a little lower being recommended so that the dissociation pressure of the halides will be at least 0.01 atmosphere.

Treatment with Metallic Copper

Treatment with metallic copper is specified in a German patent issued to Pitt and Vleck,¹⁹⁷ and in United States patents issued to Pitt,¹⁹⁶ Frasch,¹⁰⁸ and later to Cross⁶⁵ for decolorization and especially for desulfurization of petroleum, the treatment being applied in the liquid or in the vapor phase. In the latter the oil vapors are passed over metallic copper, which is preferably in the form of copper wool, the fibers of which are uniform in size and extremely fine.¹⁸³

In the liquid phase the oil is treated either to eliminate the corrosiveness or to prevent the development of acidity on standing, especially in transformer oils. In treatment of gasoline to correct the corrosiveness caused by elemental sulfur, the gasoline is passed into a tank which contains sheets of copper and is left there for 8 to 14 hours. Iron or steel turnings properly cleaned and left for several hours in a ten per cent copper sulfate solution so as to receive a deposit of fresh copper constitute an active reagent for removing elemental sulfur or hydrogen sulfide.¹⁵⁴ For the same purpose Burchard⁵⁰ recommends an apparatus consisting of a plurality of copper and zinc plates placed in the oil-storage tanks.

Oil can be freed from elemental sulfur by passing it between annular discs of sheet brass, separated by exceedingly thin masses of electrically deposited copper.⁷² More economical methods are generally used to remove elemental sulfur.

Treatment with Lead Oxide

In addition to the use of lead oxide in doctor solution, it is also used alone or in combination with copper oxide and iron oxide in the vapor-phase treatment of oils, as described in more detail in this chapter in the discussion of treatment with cupric oxide.

Frasch,¹⁰⁰ in a series of patents, refers to the use of lead oxide and other oxides, salts of metals, etc., for desulfurizing. He also gives mechanical and construction details of the process and methods of regenerating the lead oxide. Gordon¹¹⁸ specifies distillation over lead oxide, washing the distillate with magnesium sulfate, and finally purifying the oil with acid and alkalis.

One patent specifies sweetening of petroleum distillates by contacting oil vapors with an oxide of lead which has been fused with aluminum hydroxide and caustic soda.⁶⁶

Johansen¹⁴⁸ treats sour distillates with a metallic oxide, which he claims is capable of forming with the sour constituents of the distillate compounds which remain dissolved in the oil and have a tendency to suppress the detonation. The feasibility of such a process is obviously questionable.

Treatment with Metallic Lead

Claims are made that oils can be desulfurized by passing the oil vapors through molten lead or similar metals,⁵⁴ or by treating an oil distillate with an active chemical element, such as molten lead, and an inactive element, such as carbon, a final treatment with acid being given.²²⁴ However, the many practical attempts made to use the molten lead for removing stable organic sulfur compounds from light petroleum oils, even at as high a temperature as 1100° F., have ended in failure.

Treatment with Arsenic and Arsenic Compounds

As early as 1889⁷⁵ the use of arsenic and its salts was patented for removing elemental sulfur from oils. On distilling cracked gasolines from arsenic, some arsenic trisulfide is formed, but the resulting products are said to be more offensive in odor than the original oil, and they have a yellow color.¹⁷⁷ (The use of aqueous thioarsenite solution for the extraction of hydrogen sulfide from vapors in the Thylox process is described in Chapter IV.)

Treatment with Calcium Carbide

Calcium carbide is claimed, though questionably, to be effective for the

desulfurization of petroleum oils. Blackmore³¹ uses this process in desulfurizing oil; the oil vapors are passed through granular carbide, the final products of the reaction being calcium sulfide, acetylene, and olefin. It is also claimed that desulfurization can be accomplished in the liquid phase under pressure provided the temperature is sufficiently high.

Small amounts of moisture in oil are easily removed by means of calcium carbide through the formation of calcium hydroxide and acetylene.



Treatment with Calcium Sulfide

A process for removing sulfur from oils by the use of calcium sulfide and other alkaline-earth sulfides has been patented by Cobb.⁵⁹ The sulfides are known to form the alkaline polysulfides with elemental sulfur from the oils; but their practical value for other sulfur compounds has not been demonstrated.

Hydrogenation and Sulfur Removal

A decade ago it was thought that hydrogenation would be applied extensively in cracking operations in order to increase the yield of the liquid products,⁸ but the price of the crude oil has remained too low for the expensive operation to be economical. During the last few years, however, the original conceptions of hydrogenation have undergone many changes, and certain practical modifications have developed.

At present three different types of hydrogenation exist: hydrocracking (hydrogen cracking), hydroforming (hydrogen reforming), and hydrofining (hydrogen refining). Hydrocracking and hydroforming pertain to cracking, and hydrofining pertains to refining. The first two processes, as suggested by their names, are combinations of thermal cracking and hydrogenation operations; but hydrofining is refining with hydrogenation of the unsaturated hydrocarbons without radically changing their internal structure. However, in hydrofining, a certain amount of desulfurization occurs because the degree of hydrogenation is sufficient to convert the sulfur of some of the sulfur compounds to hydrogen sulfide.

The literature on the various phases of hydrogenation is very extensive, and the reader is referred to Ellis⁹² and to "The Science of Petroleum"⁸⁰ for further information. The deterrent to the more general application of hydrogenation in the petroleum industry is the large initial investment and the necessity of supplying hydrogen by expensive manufacturing processes. When these difficulties are overcome, hydrogenation will doubtless become more common, for the process is basically sound and would tend to conserve petroleum.

It has been demonstrated that valuable solvents can be obtained by hydrogenating certain petroleum fractions, and hydrofining yields products having high lead susceptibility, high saturation, good color, and other satisfactory properties usually associated with saturated petroleum fractions. Such processes are in commercial use by the Standard Oil Company of New Jersey, which company and the I. G. Farbenindustrie A.-G. were the pioneers in the hydrogenation of petroleum products.

Puchkov¹⁹⁹ has described the desulfurization of light distillates that boil below 575° F. by hydrogenation at 750 to 800° F. and under 20 atmospheres pressure with molybdenum sulfide and chromic oxide catalysts. The yield of the distillate was 98-99 per cent, and the sulfur content was below 0.1 per cent for oils boiling below 575° F.; for residuums, greater pressures are necessary.

Evans⁹⁴ desulfurizes naphtha vapors by blending them with hydrogen, heating to 840° F., and passing the gases over a catalyst, such as nickel held in place by fire-clay, condensing the vapor, and removing the hydrogen sulfide from the condensate by washing with an alkali solution.

Crude oils are desulfurized by I. G. Farbenindustrie Aktien-Gesellschaft¹⁴⁵ by treatment with hydrogen at about 570° F. and 10 atmospheres pressure with a catalyst immune to poisoning by sulfur, molybdenum trioxide and zinc oxide being indicated. Similar results are claimed by Bullinger and others⁴⁹ from passing hydrogen and oil over adsorbents impregnated with nickel (small amounts of cobalt, iron, and copper can be present with the nickel).

The oils are also decolorized, according to Haller and others,¹²⁵ when they are passed with hydrogen over powdered nickel or other metals heated to about 660° F., the hydrocarbons having previously been passed through a column of copper heated to above 660° F. Likewise the gum-forming substances can be removed by the action of hydrogen in the presence of a catalyst, such as nickel, which is kept in suspension in the liquid by agitation. The recommended temperature of treatment is from 175 to 390° F.⁶²

Franfurter¹⁰⁴ and Thomas²³⁸ claim that oils can be desulfurized by using an "outside" catalyst for activating hydrogen before it is contacted with the oil. Whenever the hydrogenating of the oils is the chief object, some desulfurization also occurs.¹⁴⁰

Treatment with Compounds of Manganese

Various compounds of manganese have been investigated and patented for desulfurizing and decolorizing oil products. The odixation is not selective; but, as with other oxidizing agents, the organic sulfides are eventually oxidized to sulfones, and the mercaptans first to disulfides and then to sulfonic acids. The sulfonic acid and to some extent the sulfones can then

be removed by washing with water, in which they are soluble.²⁰⁴ Potassium permanganate has never been used extensively because of the complications which arise, and because of its relatively high cost in comparison with other compounds which are more effective for the specific uses. Bleaching of oils with any kind of manganese compounds is of doubtful value, for the oil is almost always given a yellow-green color, which cannot be easily corrected. However, it appears desirable to report briefly the following proposals for using these compounds.

Heber¹⁸⁰ advances the idea of washing an oil with a solution of permanganate and persulfates at normal temperatures for deodorization. Another patent, issued to Stewart-Wallace,²³² claims a "purification" of oil by treatment with potassium permanganate, or other manganese compounds, with or without sodium hydroxide and in the presence of air or oxygen. In examples of the desulfurizing of oils with permanganates, Redwood²⁰⁴ shows that the sulfur content of one sample of gasoline was reduced from 0.11 to 0.027 per cent, and of another from 0.05 per cent to 0.018 per cent. Black and others²⁹ have processes for sweetening oils by treating them first with a caustic soda solution containing suspended manganese dioxide and then with an adsorbent clay at sufficiently high temperature (200 to 400° F.) to polymerize the unsaturated hydrocarbons. Sufficient pressure is maintained to prevent any substantial vaporization of the gasoline or naphtha.

As stated earlier in this chapter, the only methods of desulfurization used in a practical way over a long period of time were those employing strong sulfuric acid and liquid sulfur dioxide, the acid only being applicable to gasoline, and either reagent to kerosene and the heavier distillates. At present much energy is being directed to removing the sulfur catalytically by the aid of activated adsorbent earths or the adsorbent earth in conjunction with certain combined metals. The Houdry and Perco processes are the best examples of these developments.

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Chapter VI

Refining by Adsorption

Adsorbents are used extensively on petroleum products to remove suspended, colloidal, and dissolved impurities, such as carbon or coke, resinous and asphaltic substances, especially those rich in combined oxygen, hydrocarbons poor in hydrogen, and coloring matter, and to "neutralize" acid-treated oils without the application of alkaline solutions and washing with water. Adsorbents usually give oils greater chemical stability and resistance to oxidation, reduce their acidity, and improve their demulsifiability and other properties. Adsorbents can often be used advantageously in place of sulfuric acid or solvents. The results of refining with adsorbents and with sulfuric acid are at times very similar, though not necessarily identical. The high cost of refining with adsorbents in comparison with sulfuric acid and solvents usually prevents their exclusive use. The nature of the stock, the type of finished product, and the relative costs of refining are the important factors which determine the choice between adsorbents, sulfuric acid, and solvents, or any combination of them.

Since the beginning of the petroleum industry, adsorbents have been used in petroleum refining. They were used earlier in decolorizing vegetable and animal oils.

Adsorbents have been used for hundreds of years by the Chinese for clarifying vegetable oils.¹⁵⁰ In the United States adsorbents were first used in the soap industry and later in the petroleum industry. A number of early patents was issued for treating mineral oil products with adsorbents. Fullwood⁸⁴ used alumina or clays for refining petroleum oils as early as in 1855. Johnston¹⁵² distilled crude oils in contact with charcoal. Fordred⁷⁸ filtered oil through fuller's earth after acid and alkali treatment. The use of powdered adsorbents,²¹¹ as well as other variations of refining methods,¹⁷ was also recommended at an early date. Bierce²¹ gives a brief survey of the history of contact filtration. See also Krczil,¹⁵⁴ Fussteig,⁵⁸ and Eckart and Wirzmüller,⁶⁸ who summarize our present knowledge of active clays.

Almost all petroleum products, including crude oil itself,³ vaseline,¹⁷⁷ paraffin wax,⁷⁹ medicinal oils,⁴⁷ etc., can be bleached or decolorized with adsorbents, either alone or in combination with other reagents, though different methods are used in treating light distillates from those of treating heavy distillates, or the solid and semisolid products, etc. Adsorbents are used on light oils more generally for the improvement of color, though they are used for other purposes, such as for the removal of acid, traces

of alkalis, soaps, and certain solvents, and for the reduction of gums and, to a slight extent, of sulfur. Adsorbents often constitute the only practical reagent for neutralizing the acid-treated heavy oils because of the strong tendency of these oils to emulsify if alkali solutions are used. The adsorbents also have considerable use as catalysts for chemical reactions in the manufacture of by-products¹⁵¹ and as catalysts for cracking oils. They can be used for the prevention of "sludge" deposits in insulating oils, for dehydrating transformer oils, for purifying residual oils containing free carbon in temporary suspension, etc.

Adsorbents, such as bentonite,⁵² fuller's earth,⁵³ bauxite,¹³¹ etc., have been recommended as cracking catalysts. Charcoal, as well as other adsorbents, may be used for simultaneous hydrogenation and cracking.⁶⁰

Patents have been issued for the addition of fuller's earth to transformer oils to prevent the depositing of solids or sludge in transformers.¹⁰ Adsorbents have been used to keep transformer oils dry during storage and in transport.⁷ They may be used to recondition insulating oils, the adsorbents and the oil being previously evacuated and then contacted in absence of air.²²⁶ Activated charcoal with sodium hydroxide or sodium carbonate in a dry and finely divided state has been suggested for the same purpose.⁴⁴

Three distinctly different methods of applying adsorbents to oils have been developed: percolating the oils in the liquid state through a column of granular adsorbent materials (refining by percolation); mixing the oils in the liquid state with finely divided adsorbents and then separating them by filtering (refining by contact); and passing the oil vapors through a column of granular adsorbent materials (refining in the vapor phase). In an old method, which has recently come into use again, the oil is distilled from contact with the adsorbent in the still; this method (the Filtrol Fractionation method) may be considered a modification of the liquid contact method. All the methods are described below.

Typke²⁷⁰ surveys the literature relating to the use of bleaching earths in the mineral oil industry, and Eckart⁶⁷ gives many references to literature prior to 1928.

THEORETICAL PRINCIPLES OF REFINING BY ADSORPTION

It is now generally recognized that the removal of the undesirable constituents from the oils by adsorption follows more or less closely the general adsorption isotherm of Freundlich,⁸³ which is mathematically expressed as follows:

$$\frac{x}{m} = KC^n$$

where:

x = units of impurities removed,

m = quantity of adsorbent used,

C = equilibrium concentration of the impurities in the oil,

K and n = constants, depending on the nature of the adsorbent, substances adsorbed, and the solvent.

This equation can be converted into the logarithmic form:

$$\log \frac{x}{m} = \log K + n \log C$$

The logarithmic equation shows that the plotting of the values of $\log \frac{x}{m}$ against $\log C$ gives a straight line with a slope n , intersecting the Y -axis at a point corresponding to $\log K$. It is evident that a slight error in color readings does not appreciably affect the lower part of this curve.

The plotting of the original colors against the $\frac{x}{m}$ values seems to have no theoretical foundation.⁹⁷

Svedberg²⁰⁷ gives a historical review of the development of various adsorption formulas.

The equation indicates that fractional additions of adsorbents to an oil should be advantageous, and that refining by percolation should give better utilization of the adsorbent than direct contacting of the adsorbent with the oil, since the percolation is equivalent to applying the adsorbent in an infinite number of stages. The same equation further indicates that if two oils of different colors must be bleached and blended, it is preferable to treat them separately and then blend them rather than to blend them first and then treat them. It also indicates that the treatment of oils diluted with some inert, colorless oil would not be comparable to the treatment of the undiluted oils, and, further, that partial removal of the impurities from an oil should render the oil more resistant to further treatment.

The equation can be used advantageously for the evaluation of the relative efficiencies of adsorbents. As constants K and n depend both on the properties of the adsorbent and the oil, the relative efficiencies of the adsorbents can be compared only by investigating their effects on the same oil, since the impurities in lighter and heavier petroleum distillates or in distillates from different sources are not uniform. Thus charcoal has a very slight affinity for the colored substances in light distillates but an appreciable affinity for those in heavy oils.

The practical application of the adsorption equation for testing oils is as follows: An oil is treated with a standard clay, and the coefficients K and n are evaluated from the graph. The same coefficients are then determined for a sample of clay of unknown efficiency, and the first of the two resulting equations,

$$\frac{x}{m_{std}} = K_{std} C^{n_{std}} \text{ and}$$

$$\frac{x}{m_{un}} = K_{un} C^{n_{un}},$$

is divided by the second. The new equation,

$$\frac{m_{un}}{m_{std}} = \text{efficiency} = \frac{K_{std}}{K_{un}} C^{(n_{std}-n_{un})} = K C^{(n_{std}-n_{un})},$$

can be plotted graphically and used for evaluating the adsorbent for the particular oil.^{55, 175}

It must be remembered that in developing these equations, no account has been taken of other than the principal impurity, nor of new impurities introduced into the oil by the chemical action of the adsorbent on the oil. It is, therefore, surprising that the adsorption equation usually applies fairly accurately in practical work.^{229, 253} The irregularities in the equation become very important in the treatment of cracked distillates, for the gasoline introduces appreciable variations from Freundlich's equation if the oils are left in contact with the adsorbent for a long time. Thus the color of a cracked distillate develops rapidly in contact with the adsorbent and may finally exceed in intensity the color of the original oil, whereas the curve plotted for the same distillate left in contact with the adsorbent for only the minimum length of time may follow the adsorption equation with the regularity of a straight-run distillate.

It is thought that oxygen is primarily responsible directly or indirectly for the discoloration of cracked distillates, though polymerization reactions may also have some influence on the color, and that the various adsorbents differ in their influence on these reactions.²²⁹

In order to apply Freundlich's equation in the treatment of oils for color, the color must be expressed on a scale directly proportional to the concentration of the coloring matter in the oil. This procedure is possible by use of the color conversion tables given in the appendix. Such conversions are always only approximate and unavoidably introduce additional errors into the mathematical calculations.

Calculations have been made from Freundlich's equation as a base, and formulas have been developed which can be used in estimating clay efficiencies of continuous contacting plants.¹⁴⁹

Several theories relating to the adsorption phenomena have been advanced in an attempt to explain the adsorptive properties of clays. These theories are reviewed by Stagner.²⁴⁴ In general, it appears most probable that the adsorption is associated with the presence of hydroxyl groups directly connected to the silicon atoms in the clay.

COLOR AND PETROLEUM OILS

Several methods of measuring color have been used in the petroleum industry, but most of them are unscientific and confusing. In dealing with color it is important to separate carefully the stimulus, or effective light, from the sensation, or effect on the eye. Stimulus involves only the intensity and the wave frequency of the light. Sensation is the physiological response of the eye to the light stimulus.

All colors are produced by some combinations of frequency of vibrations and intensity of light; hence to analyze color precisely it is only necessary to determine the extent to which the various wave lengths are present in a given stimulus. (The visible spectrum ranges from about 4000 to 7000 Ångström units. The Ångström unit equals one ten-millionth of a millimeter.) However, this analysis of the stimulus does not give a description of the sensation that the stimulus produces.

In considering the sensation, a subjective scale of color must be established, which is different from the above physical scale. In arriving at this subjective scale it is necessary to agree on a standard light source, which is generally accepted as the average noonday sunlight at a latitude of 39° (Washington, D. C.) and corresponds approximately to a black body radiation at 5000° K. It is then possible to describe any color in terms of its three attributes which are defined by the American Optical Society¹⁰⁵ as follows:

"Brilliance is that attribute of *any* color which may be classed as equivalent to some member of a series of grays ranging between black and white.

"Hue is that attribute of *certain* colors which differs characteristically from the gray of the same brilliance and which permits them to be classed as reddish, yellowish, greenish, or bluish.

"Saturation is that attribute of *all colors possessing a hue* which determines their degree of difference from a gray of the same brilliance."

From the above definitions it follows that brilliance indicates how bright or how intense the color looks to the eye irrespective of whether its hue is blue, red, yellow, or green, etc. Saturation refers to the relative proportion of hue present in a given color. However, colors possessing in the standard reference light the same values of brilliance, hue, and saturation may not necessarily have the same appearance in light of a different character. This situation means that sensation produced on the eye is also dependent on the illumination, which fact necessitates the above-noted standardization of the light source.

In reference to brilliance or intensity alone, the eye does not respond in direct proportion to the intensity of the stimulus, *i.e.*, the amount of light energy present. The relation between these subjective and objective concepts of color is approximately logarithmic. Thus, if we divide the interval from black to white into ten equal visual steps, the corresponding changes in the amount of energy of the reflected or transmitted light is approximately as follows:

Visual Step No.	Light Energy, % Total
0 (black)	0
1 (gray)	1
2 (gray)	4
3 (gray)	9
4 (gray)	16
5 (gray)	25
6 (gray)	36
7 (gray)	49
8 (gray)	64
9 (gray)	81
10 (white)	100

These data indicate that a change of about one per cent in the light energy in the low-intensity end of the scale has the same relative effect on the eye as a change of 19 per cent (100% less 81%) in the light energy in the high-intensity end.

Hue is more complicated than brilliance or intensity, and its discussion is here restricted to the hues associated with petroleum colors. If a narrow band of visible spectrum is used, sensations of violet, blue, green, orange, and red are observed. However, for the same amount of light, the greens will appear much more intense

than the other colors, because the eye is more sensitive to the green light, or to wave lengths of 5000 to 6000 Ångström units. If all the colors are present in proportions corresponding to those found in the standard light source, the sensation is white, or gray, as explained in the discussion of brilliance. If there is a deficiency of color in any part of the spectrum, the color sensation is not white, or gray, but some hue depending upon the nature and intensity of the different wave lengths present. For instance, if only the first third of the visible spectrum is present, the sensation is blue-violet. If the middle third is present, the sensation is green; and if the last third is present, the sensation is orange-red. These three colors are often called the additive primary colors because they can be added to produce white or added in correct proportions to produce all the hue sensations. However, technical difficulties encountered in reproducing these pure colors have prevented development of color measuring systems based on additive colors. Instead of these additive colors, subtractive colors have therefore been generally adopted.

Subtractive colors are obtained by subtraction, *i.e.*, absorption from the white light of the additive primary colors. In this case the color sensations become entirely different. If the first third (violet-blue) of the spectrum comprising the shortest wave lengths is absorbed, the sensation is yellow; if the middle third (green) is absorbed, the sensation is pink (magenta); and if the last third (orange-red) is absorbed, the sensation is blue-green. Likewise any hue may be produced by adding such subtractive colors in correct proportions.

The transmitted colors of petroleum oils with the use of white light are subtractive because some of the light is absorbed by the oil. The absorption is also selective and is most marked at the violet end of the spectrum. In oils of increasingly higher boiling points, the hue changes from pale yellow through deep yellow and orange to red because more and more light is absorbed towards the red end of the spectrum. If the oils are brilliant and clean-looking, as Pennsylvania oils often are, the colors may be said to have high saturation; *i.e.*, not much gray is mixed with the hue. Otherwise the oils appear "muddy" and dull. Lightly refined Coastal oils, or oils containing appreciable amounts of asphalt, have this muddy appearance; *i.e.*, they possess a high gray factor and lack saturation although their hue may be the same as that of a bright, sparkling Pennsylvania oil.

The above discussion explains another complication which arises in measuring oil colors. In thin films, such as used in Lovibond colorimeters or in the Tag-Robinson or Duboscq colorimeters under certain conditions, the eye does not respond at all to the gray factor but only to the hue. Hence, two oils in thin films may have about the same appearance, whereas in thicker films one of the oils may be a brilliant yellow, and the other practically black.

Although the Lovibond system of colors is perhaps the least satisfactory from this point of view because thin layers of oil are used, all other common color systems based upon visual matching of the oil color with colored slides tend to introduce similar error depending upon the selection of the colored glasses, thickness of the oil films, and increments in the color of successive glass slides. However, a scientific system of color measurements is too complicated to be of practical use, and as a result some compromise must be made. In this respect the photoelectric colorimeter described by Story and Kalichevsky²⁵³ seems to have considerable value, for it gives a direct measurement of the relative lightness or darkness of the oil as it appears to the eye.

The petroleum industry uses either arbitrary color scales or color scales in which an attempt is made to express the readings in terms of "true" colors. These "true" or additive color scales are supposed to make possible the calculation of colors of diluted or blended samples by simple arithmetical rules. As pointed out above, this procedure is impossible in practice; at best only an approximation to the so-called "true" color scales can be made.

Another method of reporting color consists in matching approximately the hue and the color intensity of the oil with a series of colored glass discs containing com-

binations of all three basic colors. This last method is capable of reporting color in a semi-precise manner, but the length of time required for observations and the difficulty of interpreting the data minimize its practical value.

The so-called "true" color scales are usually based on the incorrect assumption of the validity of the laws of Beer and Lambert* for petroleum oils. Claims have been made that these laws are applicable to petroleum oils;^{199, 277} but this assumption is certainly not true if the colors are compared with white light,^{14, 229, 253} as is apparent from the previous discussion. For oils having relatively light color and good transmission in the green portion of the spectrum, Beer's law is reasonably accurate, but for dark oils having a proportionately greater transmission in other than the green portions of the spectrum, Beer's Law is inaccurate. Inaccurate results are also due to the peculiarities of the spectral response curve for the human eye because the visual sensation produced by the absorption of a definite percentage of light varies with the spectrum wave length. However, it is evident that Beer's Law is more or less closely obeyed if the petroleum oils are inspected in monochromatic light, though such artificial colors will not necessarily parallel the results of visual inspection when white light is used. Moreover, the different curves obtained by using different types of monochromatic light do not coincide. This condition is an additional proof of the limitations of "true" color measurements as discussed by Ferris and McIlvain.⁷⁰ It is also of interest that the ultraviolet portion of the spectrum, owing to its effect on fluorescence, may change somewhat the visual appearance of the oil.

The slow progress in the colorimetry of petroleum oils can be ascribed to the lack of precision in the definition of color units and in the confusion which results from insufficient understanding of the importance of differentiating between the various attributes of color. The various attempts to express the color sensation as a single value, such as by the use of triangular coördinates,¹⁷⁹ have been unsuccessful, owing to the difficulty of interpreting such artificial values. It seems, therefore, that the probable solution of the problem is that of expressing the color of substances such as petroleum oils by at least two independent measurements, one relating to the brilliance and the other to the hue.

A considerable amount of work has been done in developing tables for converting the color readings from one instrument into readings of another instrument. The comparison of the various color scales which is presented in the Appendix of this book is only approximate and is more of a qualitative than of a quantitative nature. This statement also applies to the "true" colors which appear in the same table.

In the following references attempts have been made to establish relationships between the different color scales:

Ferric Chloride and Cobalt Chloride Solutions and NPA colors ³⁰¹	NPA Colors and Ferric chloride and cobalt chloride solutions ³⁰¹
Stammer colors ²²⁰	Lovibond colors ⁸
Hellige Colors and Potassium bichromate solutions ²⁷¹	Potassium bichromate solutions ²⁷
Stammer colors ²⁷¹	"True" colors ²²⁹
Wilson colors ²⁷¹	Photoelectric Colors and Iodine colors ²⁵³
Iodine Colors and Photoelectric colors ²⁵³	Potassium Bichromate Solutions and Hellige colors ²⁷¹
Tag-Robinson colors ²²³	NPA colors ⁵⁷
Lovibond Colors and NPA colors ⁸	Saybolt colors ⁵⁷
"True" colors ¹⁹⁹	Stammer colors ²⁷¹
	Wilson colors ²⁷¹

* Laws of Beer and Lambert assume that for equal intensities of transmitted light, the concentration of coloring matter is inversely proportional to the thickness of the absorbent layer.

Saybolt Colors and Potassium bichromate solutions ⁵⁷ "True" colors ²²⁰	"True" Colors and Lovibond colors ¹⁹⁰ NPA colors ²²⁰ Tag-Robinson colors ²²⁰ Saybolt colors ²²⁰
Stammer Colors and Ferric chloride and cobalt chloride solutions ²²⁰ Hellige colors ²⁷¹ Potassium bichromate solutions ²⁷¹	Union Colors and Tag-Robinson colors ²⁰
Tag-Robinson Colors and Iodine colors ⁵³ "True" colors ²²⁰ Union colors ²⁰	Wilson Colors and Hellige colors ²⁷¹ Potassium bichromate solutions ²⁷¹ Stammer colors ²⁷¹

CLASSIFICATION OF ADSORBENTS

Since various adsorbents are used for treating petroleum products, the proximity of natural deposits determines to some extent the selection of the adsorbent by a refinery because of transportation costs. In general, however, the use of a more efficient adsorbent, even if more expensive, is more economical than the use of a less efficient and cheaper one. A careful economical balance must, therefore, be made before the adsorbent can be selected.

Adsorbents may be divided into two general classes: those derived from living organisms, and those of mineral origin. The first class is mainly composed of the different grades of animal, vegetable, and the so-called mineral charcoals, which were used to a limited extent in the early petroleum industry, but which are now almost completely superseded by the cheaper, more efficient adsorbents of mineral origin. The activated carbons, as stated above, have only slight affinity for the coloring matter in light petroleum distillates but more affinity for the darker-colored substances in the heavy oils. Many patents have been issued for the use of activated carbons in decolorizing mineral oils; but they are now mostly of historical interest, and their full description is not warranted. A few plants still use charcoal for the decolorization or deodorization of some special products, such as waxes. However, it is doubtful whether those adsorbents can long withstand the competition offered by the more efficient clays.

Lewis¹⁰⁷ in an old patent specifies bone black, blood charcoal, and other similar adsorbents for refining petroleum products; Chesebrough recommends a combination of bone dust, pulverized oyster shells, and cotton cloth,⁹⁰ or bone black and peat charcoal;⁴⁰ Huot¹²⁰ separates the bone black from the oil by centrifuging; Van Wyck²⁷⁰ uses carbonized animal matter deposited on chalk; Sylvester²⁵⁸ passes the oil through hot water and then purifies it with bone black; Field⁷⁷ treats wax in naphtha solution with charcoal and then distills off the naphtha; Horne¹²³ refers to various patents issued on the use of bone black and decolorizing carbon by the industry; Smith²⁴² patented a special apparatus designed for treating oils with charcoal; Vander Weyde²⁷⁵ filters the oil through a bed of charcoal; Stewart²⁵¹ specifies an oil filter containing charcoal, sand, and other materials; Johnston¹³³ distills the oil in contact with charcoal; Neiman¹⁵⁰ uses a filter containing layers of charcoal, lime, and woolen cloth;

Richter²²² uses activated carbon for deodorizing oils; Collins⁴ uses charcoal for similar purposes; Cumming⁵¹ recommends carbon black; Shachovtzev²²⁷ investigated the decolorizing efficiency of powder obtained from potassium ferrocyanide and animal waste after washing with water and hydrochloric acid; Internationale Bergin Co. voor Olie en Kolen-Chemie¹³⁰ patented the use of coke ash; Chesebrough¹¹ filters Vaseline through charcoal; Ujhely and Beurle²⁷² treat ozocerite with fuming sulfuric acid and then with bone black; Gray²² filters paraffin through bone black; Macherski and Koperski¹⁶⁶ filter the oil through bone black mixed with sodium carbonate and zinc powder; Engler and Höfer⁷¹ enumerate a number of processes for treating petroleum oils with charcoal and allied substances and state that the use of carbon in refining oils dates back to 1862.

More recently attempts have been made to use the charcoal or activated carbons mixed with clays or mineral gels for decolorizing oils. Such mixtures are claimed at times to have better adsorption power than the individual components; thus a mixture of carbon and alumina gel is said to possess special affinity toward the sulfur compounds in petroleum oils.⁴² Similar claims are made for a combination of carbon black and silica gel or china clay.⁵¹ Successive treatments with diatomaceous earth and carbon are reported to be more efficient in certain cases than the use of either separately.²⁸¹

Vegetable fibers, such as sawdust, have even come into use in the oil industry, but usually for purposes other than bleaching. The sawdust is used primarily for adsorbing the last traces of acid left in the oil after sulfuric acid treatment and is not intended as a final finishing procedure,⁹⁴ but patents have mentioned sawdust and lime for final treatment of oils.⁶⁰

Adsorbents of mineral origin have been prepared synthetically, but commonly they are found in nature and are used in their natural state or after treatment with acid to enhance their adsorptive properties. The synthetic adsorbents include silica gel, alumina gel, ferric hydroxide gel, or their combinations. Of these synthetic adsorbents, silica gel is best known, but it is used to a very limited extent for refining petroleum products; the high cost of such adsorbents hinders their wide use.

Synthetic adsorbents consisting of mixtures of two or more gels have also been recommended at various times. Compounds of definite composition have been patented, such as $\text{Al}_2\text{O}_3 \cdot 12\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.⁴³ Other patents specify mixtures, such as those of alumina and silica in activated condition.²⁵⁰ It is important to choose the proper base on which the synthetic adsorbent is to be precipitated if the base is desired for strengthening the structure of the gel, etc. Thus silica gel precipitated on alumina gel is said to be very active, but silica gel precipitated on other inert materials is inactive.⁴²

A large quantity of natural mineral adsorbents is used in the refining of petroleum. It is estimated that over 97 per cent of the annual production of bleaching earth is thus consumed. In the United States the chief

sources of these bleaching earths are Georgia, Florida, Southern Illinois, Texas, Colorado, Utah, Arizona, and Southern California. Several of the plants produce as much as 10,000 tons per month each. There are also deposits of bleaching earths in England near London, in various parts of Germany and Russia, etc.

The bleaching earths and clays are believed to be the intermediate degradation products from igneous rocks, such as granite, basalt, diorite, diabase, etc.¹⁸⁹ Because of the large supply, cheapness of mining, and ease of pulverizing, only the sedimentary deposits of the bleaching clays are now being worked in the United States.

The natural mineral adsorbents may or may not require chemical treatment. Those given chemical treatment are more expensive for use on petroleum, and they encounter serious competition from the untreated adsorbents. However, the chemically treated adsorbents are often more economical to use, for less clay is needed, less oil is lost, and the operation costs are lower.

The more important of the mineral adsorbents are: the various fuller's earths, bentonite,^{189, 295} various clays,^{192, 249} magnesite,¹²² bog iron ore,¹²⁹ bauxite or alumina,²¹⁰ bituminous shale, etc.²²⁰ Many of these are sold under trade names, such as "Decomat",¹⁸¹ "Filtrol," "Superfiltrol," "Milwhite," "Tonsil," "Wilkinite," "Palex,"¹⁸³ "Porocel," "X-YTE," etc. Their relative values for refining should be determined experimentally. Mixtures of different adsorbents have also been patented.¹

Methods of Preparation

The efficiency of many of the adsorbents depends largely on their method of preparation. This condition is true of the mineral as well as of the carbon adsorbents. Their original source and method of treatment affect very differently their porosity and consequently their adsorbent power.

Synthetic adsorbents, such as silica gel, may be prepared in different ways, and their efficiencies likewise vary with the method of preparation. Commercial silica gel has long been advocated as a good refining agent,²³² at least for some of the petroleum products, although for decolorization of lubricating oils its value is sometimes questionable.³⁰ During the past fifty or sixty years many methods of producing silica gel have been devised. It can be prepared by precipitating water-soluble silicates with acids or with the acid salts.^{190, 241} At present it is chiefly made by precipitating the soluble silicates with sulfuric acid,¹⁷⁸ drying the precipitate carefully, preferably by applying moist heat,¹¹⁸ and crushing it to produce particles of the desired size. The methods are all expensive, and for this reason the use of silica gel is very limited in petroleum refining.

The preparation of alumina gel is usually similar to that of the silica gel.

The gel can also be prepared from granulated aluminum and water by the catalytic action of a small percentage of aluminum amalgam, and this product is claimed to possess superior activity.²⁹⁶ However, the synthetic adsorbents are now of but little practical interest in decolorizing petroleum oils, though they are widely used in other fields of petroleum chemistry, such as in catalytic cracking and reforming operations.

Natural adsorbents are sometimes merely dried in the sun and crushed to the desired degree of fineness before they are used on the oil. The Death Valley clays of California are examples of such adsorbents. Some of the natural adsorbents which are to be used on light oils at normal temperatures require ignition, or "tempering," at 500 to 900° F. in order to expel nearly all the water which they contain. As pointed out later, the water content is a variable factor in the bleaching power of fuller's earth. The amount of moisture which should be left in an adsorbent varies both with the adsorbent and with the oil treated. Some adsorbents decolorize equally well before and after the removal of the moisture, but others lose some of their bleaching power when all the moisture is expelled.¹⁴¹

If the clays are to be heated, they are now usually "burned" to a predetermined temperature rather than to a definite shade of color, as was the earlier practice. This control provides a much better "tempering" operation and greater uniformity. Burning clays at high temperatures results primarily in loss of moisture, though other changes may also occur. Too much heating permanently impairs the internal structure of the adsorbent. The efficiency of some adsorbents can be improved by washing them with water prior to drying,¹⁰ or by steaming them.²⁷⁸

The powdered contact clays can be applied to the oil either in a dry or in a moist or wet condition. If the clay contains moisture, the mixed oil and clay are heated enough to expel the water,²¹³ and the released moisture displaces the air from the oil and adsorbent, a feature which improves the activity of the adsorbent, other things being equal. It is best to use the adsorbents when freshly prepared and before they adsorb impurities that can lower their decolorizing power. The fine-mesh contact clays are generally stored in more or less water-proof bags to protect them to a certain extent from contact with the atmosphere. The adsorbents may be applied to lubricating oils as a very wet slurry of clay and water; but the clay is in general used in this condition only by the refiners who activate their own clay, because the clay usually cannot be shipped economically in the water-wet slurry. This wet clay obviously is applicable only to the heavy oils, such as the lubricating oils that are to be bleached at elevated temperatures. Adsorbents used in percolation or in treating light distillates at normal temperatures are most efficient when the moisture content is low and within a rather narrow percentage range. Such clays should be pro-

tected from the atmosphere as much as possible. The coarse percolation clays show their highest efficiency when they are freshly ignited and charged to filters while still warm.⁶⁴

The efficiency of certain adsorbents is improved and the time of contact for decolorization lessened by activation with acids or by the addition of certain chemicals. This property of increasing the rate of decolorization is of special advantage in the continuous contact treatment of light oils, for in this treatment the time of commingling is usually short. This time factor in the selection of the adsorbent or in its application is often overlooked. Two different samples of clay may decolorize an oil equally well in a long time of contact but may give entirely different results in a short time.

The most efficient adsorbents are usually prepared by treating the natural clays with dilute sulfuric or hydrochloric acid; ^{54, 160} sulfuric acid is commonly used in the United States, and hydrochloric acid in Germany and some of the other European countries. The concentration of the acid and the method of treatment must be adjusted for each individual clay deposit, but in general the concentration of the acid is about 20 per cent. After leaching with acid, the clay is washed with water and usually dried, although sometimes the wet activated clay is added directly to a lubricating oil, as noted above.

The acid treatment of the clays improves their activity. Some clays which are inactive in the natural state can be activated by this treatment considerably more than clays which have decolorizing properties in the natural state. The decolorizing power of the raw clay is thus not an indication of its efficiency after it is subjected to the chemical treatment. Stagner²⁴⁴ discusses the methods used for activating clays with sulfuric acid. It is pointed out that the highest adsorbent activity is usually imparted to clays that have little or no activity in their natural state.

The activation of adsorbents with acid is an old process; a German patent,²⁰² issued in 1919, was annulled because certain features of the process had been used in Germany since 1910.²¹

The chemicals added to adsorbents to improve their decolorizing efficiency are usually acidic in nature, such as aluminum sulfate, zinc chloride,¹⁴⁷ and aluminum chloride.²¹⁰ However, such additions are not in extensive use because the extra expense is not justified for all clays.

Some of the chemicals which have been advocated for enhancing the decolorizing and desulfurizing power of the clay are: the salts of copper, iron, lead, manganese, zinc, or other metals which have an affinity for some of the sulfur compounds,⁵⁰ magnesium hypochlorite or double salts of magnesium and aluminum hypochlorites,²³⁴ calcium chloride with magnesium hydroxide and chlorine,²⁸⁴ cupric sulfate and calcium hypochlorite,⁹⁵ alu-

minum sulfate and calcium hypochlorite,²⁴ sodium sulfate, or other soluble sulfate of an alkali-forming metal, and calcium hypochlorite,²⁴ finely divided metals, such as copper and nickel,¹⁵⁰ etc. However, none of these methods of removing the sulfur compounds has been practical.

Physical and Chemical Properties

Mineral adsorbents vary in their true specific gravity from 1.75 to 2.5, and in hardness from very hard to very soft. Their colors are white, brownish, bluish, grayish, or black. Gurwitsch¹⁰¹ gives the following tabulation of the general chemical composition of the Florida clays or fuller's earths:

	Per Cent
SiO ₂	44.0 to 72.0
Al ₂ O ₃	5.0 to 33.0
Fe ₂ O ₃	1.2 to 15.0
CaO	0.3 to 7.4
MgO	0.4 to 4.3
K ₂ O and Na ₂ O	0.4 to 8.3
H ₂ O	4.3 to 25.0
P ₂ O ₅ , SO ₃ , etc.	small quantities

In general, the chemical analysis gives little or no indication of the decolorizing power of these clays. However, it is accepted that alumina and silica are the active ingredients. Relatively large amounts of lime and magnesia may lower the decolorizing power of clays, an effect due mainly to the neutralization of acids and to the inertness of the lime and magnesia themselves as decolorants.²¹⁴ On the other hand, some investigators find no relationship between the magnesia content of clays and their adsorptive power.⁷³ Similar inconclusive and often contradictory statements are found in the literature regarding the presence in the clays of compounds of iron, sodium, potassium, and other elements exclusive of alumina and silica. X-ray examinations seem not to give much information concerning the structure of adsorptive clays.¹¹⁶

Considerable interest has been revived in bauxite, which is aluminum oxide found in nature. Bauxite usually contains from 60 to 85 per cent of alumina, 5 to 25 per cent of silica, and 1 to 25 per cent of iron. In addition bauxites usually contain from 2 to 4 per cent of titanium. Bauxite is sold under such trade names as "X-YTE," "Porocel," etc.

The most important deposits of bauxite in the United States are in Arkansas, but there are appreciable quantities in Alabama, Tennessee, and Georgia.

Although attempts have been made to show that the alumina content is directly related to the decolorizing power of bauxite, enough exceptions occur to disprove this theory.¹²⁵ Such correlation may hold for samples from the same deposit, but not for samples from different deposits. In general it

is believed, however, that alumina supplies to bauxite its adsorptive properties, and the silica supplies the mechanical strength. Iron and titanium contribute nothing to the bleaching power of bauxite and are regarded as inert fillers, which are preferably removed from the bauxite during the crushing operation in order to improve the intrinsic decolorizing power per unit of the adsorbent. The apparent density of bauxite of 30/60 mesh is approximately 1.0, or about twice the apparent density of fuller's earth. This difference in density of bauxite and other clays is a factor in evaluating the adsorbents. All are sold on weight basis, but their efficiencies are usually compared on volume basis. Although it is impossible to give accurate comparisons between the decolorizing power of bauxite and fuller's earth because of the variations in different oils being bleached, nevertheless the efficiency of bauxite usually approaches that of the fuller's earth on the volume basis rather than on the weight basis. The granular bauxite used to bleach lubricating oils by percolation withstands the high regeneration temperatures better than fuller's earth. This characteristic is described in detail later in this chapter.

The moisture content of bleaching clays is important. The efficiency of the clay is vitiated by too much or by too little moisture. The optimum moisture content for percolation clays is about one or two per cent. A greater amount is permissible in contact clay for decolorizing gasoline or kerosene. Lubricating oils or other petroleum products which are treated at temperatures high enough to expel the moisture frequently respond best to clays having from 10 to 12 per cent, and sometimes as high as 20 per cent, moisture. Water may even be added advantageously to the adsorbent when sufficient heat is used to expel it from the mixture of oil and clay. When water is completely expelled from some of the contact adsorbents, they become useless for bleaching vegetable oils, though they may yet possess a certain bleaching power for mineral oils.²⁹¹ It can thus be stated as a generalization that the water content of new mineral adsorbents for use in treating light oils by contact varies from 5 to 15 per cent; and the water content of adsorbents for use in treating lubricating oils at temperatures from 250 to 300° F. usually varies from 5 to about 20 per cent. If there is over 20 per cent of moisture in the raw or lump clay, difficulty is likely to be encountered in the grinding process, for the clay may adhere to the grinding equipment. The moisture of most contact clays for use on lubricating oils cannot be reduced below about 5 per cent without impairing the decolorizing power, although the moisture in granular percolation clays and in some contact clays for use on light oils can be reduced to 1 per cent or less without serious injury to their decolorizing power.

Contact clays are usually pulverized so that over 95 per cent passes through a 200-mesh screen; much of the clay is finer than 300-mesh. The

fine division is usually beneficial in increasing the rate of decolorization, although if some of the clay is too fine, it may retard the filtering operations, and it may be necessary to mix a filter-aid with the clay to hasten the filtering rate. Percolation clays are coarser, as discussed later under Refining by Percolation. In preparing materials of definite particle size for percolation, much of the material is lost to fines, which are not always utilized. Thus in crushing bauxite to particles of sizes 10/90 mesh, the loss of the material to fines is 20 to 25 per cent.¹⁹¹

The untreated adsorbents may have an acid, an alkaline, or a neutral reaction. Most fuller's earths give a distinct acid reaction with litmus and phenolphthalein. It has been shown that the various earths, when finely pulverized and suspended in water, require for titration from 0 to 275 cc. of 0.1*N* sodium hydroxide solution per 100 grams of clay when phenolphthalein indicator is used.¹⁹⁷ The range of acidity is thus very large. However, the acidity of an adsorbent is not a measure of its decolorizing power. An alkaline reaction is shown by certain fuller's earths and Death Valley clays.^{60, 175}

Some of the clays, when in suspension in water or in oil, migrate to the positive electrode under the action of an electric current.

Methods of Testing Efficiency of Adsorbents

It is usually desirable to evaluate the efficiency of an adsorbent in terms of a standard adsorbent by determining the relative amounts of the two required to refine a certain oil. The experimental procedure is generally a reproduction in the laboratory of the commercial process, including other refining treatments besides that with the clay if any are used.

The official test of the American Oil Chemists' Society specifies the use of a standard fuller's earth, which can be obtained on request.¹⁰⁰ However, this earth is standardized in terms of vegetable oils and not petroleum oils.

The usual procedure for determining the decolorizing power of contact clays for gasolines or kerosenes is to add a measured quantity of the clay to the oil and agitate the mixture mechanically or with air, the method of agitation depending on that used in the refinery. After the oil-clay mixture is agitated for the time required to give the maximum decolorization in the given type of equipment, the clay is filtered from the oil, and the properties of the oil determined in the usual manner.

The above method when applied to hot lubricating oils should be conducted so as to exclude air. A satisfactory apparatus for this purpose is described by Kalichevsky and Ramsay.^{86, 140} The oil and clay are heated while mechanically agitated to the desired temperature in an atmosphere of an inert gas, preferably steam, and then filtered. Special precautions are

taken to avoid contact of the oil with air at the high temperatures, as otherwise accurate comparisons are impossible because of the air oxidation.

In evaluating percolation clays, tests are made with laboratory percolators. In order to lessen the danger of channeling, the depth of the laboratory filters should be at least 2 or $2\frac{1}{2}$ times their diameter, and should be at least fifteen inches. The clay is properly tamped down, and sufficient bleaching time, or "soaking" time, is allowed for the different and successive samples to pass through. Somewhat less time may be allowed in the laboratory than in the plant without impairing the accuracy of the results. The percolation filters are commonly surrounded with a constant-temperature bath.* The practice of making percolation tests in heated rooms is not satisfactory because the oil percolating through the filter is kept for a relatively long time at elevated temperatures.¹⁸⁷

The above methods of evaluating the efficiency of adsorbents are the most practical. The oils must be treated in the same acid or neutral state as they are in the refinery, inasmuch as different adsorbents are activated by the acid in the oil to different extents, and an adsorbent which is efficient on a neutral oil may not be efficient on an acid oil or vice versa. Moreover, the traces of soaps or salts left in a neutral oil may seriously affect a very efficient clay and yet have very little effect on an average clay.

In evaluating adsorbents a number of stocks should be used in the experimental work, particularly light and heavy oils, since the efficiency may vary with different oils. In such evaluations the mesh of the adsorbent, its apparent density, and its moisture content are determined. Laboratory methods have been developed for these purposes.⁸⁷ When lubricating oils are being used, it is desirable to determine, in addition to the color measurements, all the other characteristics of the bleached oil, such as the acidity, ash content, demulsifiability, resistance to oxidation, etc. The optimum temperature should be determined, particularly for lubricating oils. Usually the decolorizing efficiency of clays improves with temperature. However, at very high temperatures some cracking or polymerization reactions may take place and give poorer colors if the time of contact is unnecessarily long.

Sometimes the acidity or alkalinity of the adsorbents, the filtering rate, and the amount of oil retained by the adsorbents are determined.²⁷⁰ Usually, however, all the clays have about the same retention capacities for the oil; about one unit weight of oil to two units of clay. Moreover, after the clays are used in treating lubricating oils, the oils are thoroughly washed from the clay with naphtha so that the loss of valuable oil to the clay is reduced.

The proper evaluation of adsorbents is a laborious task. Many methods

* The Research and Development Department of the Attapulugus Clay Company has recently published detailed procedures for testing adsorbents.ⁿ

have consequently been proposed as substitute tests on other bases than actual percolation or contact operations. In general these tests are not reliable, since the efficiency of clays varies for different oils, and such variations become much greater when other substances are substituted for the oil, or when some arbitrary property of clay is measured and expressed as a function of the bleaching power. However, some of the methods have shown a little merit and have been used. For example, the rise in temperature when an adsorbent is mixed with certain highly reactive chemical substances, such as pinene, acetone, or the oil itself, is used as a measure of the efficiency of the adsorbent. The efficiency of bauxite has thus been approximated by measuring the rise in temperature when the bauxite is mixed with kerosene.

For measuring the rise of temperature on mixing the adsorbents with various substances, an apparatus known as the "ergometer" has been developed. It consists of a cylinder $1\frac{1}{2}$ inches high and $1\frac{1}{2}$ inches in diameter suitable for holding approximately 50 grams of adsorbent (bauxite). The adsorbent is added, and the bulb of the thermometer placed in the center of the apparatus. The temperature is noted before and after the addition of the liquid (20 cc. of kerosene with bauxite), and the rise in temperature recorded. It is claimed that efficient bauxite gives a rise of 28.8°F. , and that a regenerated bauxite may give a rise of only 21 to 25°F. ¹⁸

The terpenes, such as pinene, have been used instead of oil for determining the temperature rise.^{18, 214} Briefly, the procedure for testing clays with pinene¹⁶ is to note the temperature rise when 5 cc. of pinene is added to 2 grams of clay in an apparatus similar to the ergometer.

Tests based on the adsorption of various dyes from solutions are unreliable,²⁵⁹ though the adsorption of methylene blue¹¹⁴ or of malachite-green from aqueous solution¹⁵ may give some indication of the value of an adsorbent. In general, the slopes of the adsorption curves for light-colored oils, especially those for kerosene, deviate very considerably from those of the adsorption of pure compounds from solutions.²²⁹

The relationship between the chemical constitution and the decolorizing power of the adsorbent materials has been thoroughly investigated, and practically none has been found to exist. However, physical examination of the adsorbent is of more value than chemical examination, as it shows the fineness, porosity, etc.; but the only significant test for the clay is its behavior on the oil. The tendency of clays to swell in contact with water is not indicative of their adsorbent power.⁵⁴

In general a highly efficient adsorbent is desired for reasons of economy. An adsorbent of low efficiency must be used in large quantity, a requirement involving more labor, storage, transportation facilities, and larger equipment for processing; but the most important factor is that, because an adsorbent of low efficiency must be used in larger amounts, the amount of oil retained by the clay is much greater. The problem of finding adsorbents of high efficiency was not simple a few years ago; from 2500

samples of earths submitted to one laboratory, only a few were of commercial value. The quality of different deposits of clay is now better standardized, the deposits of better grade being fairly well known.

EFFECT ON THE OIL

Adsorption of Hydrocarbons

Under the action of some of the active adsorbents, hydrocarbons can be adsorbed and certain of the reactive unsaturated compounds polymerized, especially at elevated temperatures. As a rule, the unsaturated hydrocarbons are the most readily adsorbed, the aromatics next, the naphthenes third, and the paraffins least. There are, however, exceptions to this general rule, as within the same class of hydrocarbons the adsorption increases with increase in molecular weight and complexity.⁹⁸ This rate of increase in susceptibility to adsorption with increase in molecular weight is, moreover, different for the different classes of compounds.

As just mentioned, the unsaturated hydrocarbons not only are adsorbed but may also be polymerized, a property which in part accounts for increase in "end boiling point" of petroleum distillates, especially of those produced by cracking, after they have been treated with adsorbent materials.¹²⁸ The degree of reactivity of the various unsaturated hydrocarbons differs, however, from one series to another. Hydrocarbons of the acetylene and pyrrole series, for example, were not polymerized after being in contact with floridin for two years, and the tendency toward polymerization within the ethylene series is different for different members.¹⁵⁶

Egloff, Schaad, and Lowry,⁷² in a broad review of the decomposition and polymerization of olefin hydrocarbons, show that fuller's earth, such as floridin, under pressure slowly polymerizes propylene to dimers, trimers, and even higher polymers; isobutylene in contact with floridin is polymerized rapidly at room temperature, and some polymerization occurs even at -112° F. Trimethyl ethylene (amylenes; boiling point, 104° F.) at room temperature and with an equal weight of dehydrated floridin is polymerized in two hours to the extent that 15 per cent of the hydrocarbon boils above 212° F., and in two days all of it is polymerized. Nearly all of the polymerized product is diamylene.

All the unsaturated hydrocarbons have a tendency to be retained by the adsorbent.²³⁰

Aromatic hydrocarbons can be separated from the usual hydrocarbon solvents by such adsorbents as fuller's earth, silica gel, etc., so that sometimes it is possible on a laboratory scale to separate the aromatics from paraffins and naphthenes by filtering the oil through a large amount of these adsorbents.¹⁶⁸ Similarly, this characteristic of adsorbents for removing

from the distillate certain groups of hydrocarbons in preference to others can be utilized with some degree of accuracy for analytical purposes. It is thus reported possible to distinguish between a Pennsylvania petroleum, which contains chiefly saturated hydrocarbons, and a petroleum which contains large amounts of non-paraffin hydrocarbons.²⁰³

The adsorption of certain classes of hydrocarbons from an oil when the oil is passed through a column of adsorbent material produces changes in the properties of the oil known as Day's phenomenon. The separate filtrate fractions collected from the filter column differ in specific gravities, viscosities, sulfur content, boiling points, etc. Thus when a crude oil is 0.912 sp. gr. was filtered through fuller's earth, the gravities of successive fractions of filtered oil were 0.8695, 0.8820, 0.9025, and 0.9040, respectively. The most viscous constituents of the oil are held the most tenaciously;⁹¹ the lighter oil retained by the adsorbent is, as would be expected, displaced first by washing exhausted adsorbents or filters with water.

Table 50. Viscosity and Gravity Effects in Percolating a Spindle Oil Through a Large Volume of Fuller's Earth (Data Pertain to the Percolate).

Barrels Percolated Through	Saybolt Viscosity at 70° F.	Gravity Bé.
1 to 5	187	31.5
5 to 10	220	29.7
10 to 15	242	28.6
15 to 20	253	28.2
20 to 25	260	27.9
25 to 30	265	27.6
30 to 35	266	27.5
35 to 40	268	27.3
40 to 45	271	27.3
45 to 50	273	27.2
50 to 55	274	27.2
55 to 60	274	27.1
60 to 65	275	27.1
65 to 70	275	27.1
70 to 75	277	27.0
75 to 80	277	27.0
80 to 85	278	27.0
85 to 90	278	27.0
90 to 100	278	27.0
Average of first 25	224	29.6
Average of first 50	246	28.4
Average of first 75	258	28.0
Average of first 100	259	27.8

The viscosity of a light oil or a partly refined lubricating oil is not greatly reduced by treatment with adsorbents.^{2, 141} Thus the filtering of "Nujol" through a relatively large volume of fuller's earth caused an average reduction in viscosity of 0.5 per cent.²² However, in the application of a large amount of adsorbent to an unrefined lubricating stock, the change in viscosity, which is primarily due to the removal of asphaltic substances,

is appreciable. The first portion of oil passing through a filter column of fuller's earth is affected much more than subsequent portions, and eventually the adsorbent does not affect the oil. Table 50 shows the data on the viscosity and gravity of successive aliquot portions of five barrels each of spindle oil stock percolated through fuller's earth in the ratio of 100 barrels of oil to 25 tons of earth.^{273, 214}

Because of the partial removal of aromatic compounds, the burning test of kerosene is improved by refining with adsorbents; but usually the effect is so slight that if the kerosene stock is rich in aromatic compounds, the use of sulfuric acid or, particularly, liquid sulfur dioxide is much more economical.

Because the paraffin hydrocarbons are least adsorbed by the clay, and compounds like the aromatics more highly adsorbed, the pour point of the oil is usually raised by percolation. Exceptions to this effect are known. Thus it has been found that on contacting a certain steam-refined stock with clay, the pour point was reduced from 50-60° F. to 14-20° F.²⁷⁹ This reduction may be due to different causes; it could be explained by the removal of asphaltic materials from the oil, as asphaltic materials may raise the pour point of an oil, or by the modification of the structure of wax crystals in the oil. Reductions in the pour point attributable to the second cause occur when the oil containing wax is contacted with clay at elevated temperatures. Some of the Pennsylvania crude oils, for instance, exhibit this property. The pour point of the oil contacted at elevated temperatures with clay may show a considerable lowering if the oil is tested soon after the clay is applied; but on standing, the pour point reverts to normal, an indication that the structure of the wax crystals has undergone a change. This subject has been discussed by Kalichevsky.¹³⁷

Adsorption of Resinous and Asphaltic Substances and Coloring Matter

Resinous and asphaltic substances are strongly reactive toward adsorbents, a property which is utilized in treating the oils for color and sometimes in removing pitchy substances from cracked oils¹¹³ or for general purification purposes.²⁶³ For instance, floridin adsorbs up to 12 per cent of its weight of this type of compound; and nine to ten per cent of the compounds adsorbed cannot be extracted from the clay even with a large excess of benzine.¹⁰¹

Practically all petroleum derivatives, including such highly refined products as medicinal oils,⁴⁷ can be decolorized by adsorbents, though under certain circumstances the use of other refining agents or combinations of them is cheaper, or may yield desired qualities in the oils impossible to secure with clay alone.

The oil should not be left in contact with adsorbents and air after the

development of the maximum decolorization, as a reversion in color will result because of various polymerization and oxidation reactions catalyzed by the adsorbents. Cracked distillates are especially susceptible to these reactions, and their discoloration on long contact has been found to be due to adsorbents acting as oxidation catalysts.^{63, 229} Rogers, Grimm, and Lenmon treated samples of a cracked kerosene of 5 Saybolt color with fuller's earth, 10 grams per 150 grams of oil, in atmospheres of four different gases and for two different periods of time, 10 minutes and 65 hours. With agitation for 10 minutes, the color in all four tests was improved; but with contact for 65 hours, the colors reverted seriously when air or oxygen was present, but not when nitrogen or carbon dioxide only was present. The data are shown in Table 51.

Table 51. Color of Cracked Kerosene in Saybolt Units after Contact for 10 Minutes and for 65 Hours with Clay in Different Gases.

Time of Contact	Air	Oxygen	Nitrogen	CO ₂
10 minutes	19	18	21	21
65 hours	12	0	21	20

The above investigators found, however, that different clays behaved differently in this type of experiment. The effect of the time of contact on

Table 52. Effect of Time and Temperature on Color of Oil in Contacting Acid-Treated Mid-Continent Cylinder Stock with Adsorbent Clays.

Treating ° F.	Temp. (° C.)	Activated Clay A ^a		Activated Clay B ^b		Natural Clay ^c	
		Time at max. temp. (Min.)	Color intensity	Time at max. temp. (Min.)	Color intensity	Time at max. temp. (Min.)	Color intensity
500	(260)	0	322	0	440	0	255
		5	260	5	320	10	180
		10	205	10	280	30	165
		20	192	20	285	60	165
		30	170	30	260	200	185
		45	165	60	210
		75	137	120	192
		120	125	200	165
		200	125
		0	163	0	245	0	160
600	(315.6)	5	135	5	170	10	136
		10	112	10	153	20	125
		20	98	20	130	30	125
		30	91	30	130	45	125
		60	84	120	92	90	108
		120	76	200	94	120	105
		200	76	200	108
		0	108	0	145	0	146
700	(371.1)	5	82	5	113	5	136
		10	77	10	95	20	119
		20	66	20	95	30	119
		30	66	30	86	60	132
		90	68	90	84	90	119
		130	112
	
	

^a 3% by weight.

^b 4% by weight.

^c 8% by weight.

the color of an acid-treated Mid-Continent cylinder stock contacted with constant quantities of clay at different temperatures was studied by Kalichevsky and Ramsay.^{86, 140} The results are shown in Table 52.

As shown under the theory of adsorption, the degree of decolorization of oils is not directly proportional to the quantity of the adsorbent used; for this reason it is often economically impossible to decolorize an oil completely, particularly a heavy oil, by means of adsorbents alone. The decolorizing efficiency of powdered adsorbents for a heavy oil, such as a lubricating oil, is often improved with an increase in the temperature of treatment. This improvement in the efficiency has been observed with practically all acid-treated clays and with a few of the natural clays. The rule is not strict, however, and in special cases the opposite may be true.

In percolation processes the oil is usually kept at a temperature as low as is consistent with good contact.²¹⁴ However, this practice is not generally recommended because the higher temperature reduces the viscosity of the oil during the treatment and thus affords much better contact between the oil and the clay and a better filtering rate. This thinning effect is sometimes attained by diluting the oil with naphtha. However, the results of straight percolation and percolation in naphtha solution are not necessarily identical. Some stocks darken readily at high temperatures, and in them a certain reversion in color may occur when the naphtha is distilled from them. The best treating temperatures must, therefore, be determined experimentally.

Light distillates, gasoline and kerosene, are practically always treated with adsorbents at ordinary temperatures unless they are treated in the vapor phase, as in the Gray process. Sometimes it is more economical to treat light oils with the adsorbents to a given initial color before they age for any considerable time because the color developed in storage is often very difficult to remove. More clay than actually required to yield a certain initial color is necessary for the fresh distillates if they are to remain colorless for any appreciable time.

Adsorption of Sulfur Compounds

Some adsorbents have an affinity for certain sulfur compounds in oils, though the quantity of adsorbent necessary to effect any marked reduction in the sulfur content is usually prohibitive. Bauxite and silica gel have been patented for desulfurization.⁶⁵

It can be definitely stated that if only an adequate amount of acid and contact clay is used on a cracked gasoline to decolorize it, there will be no reduction in the sulfur content unless the gasoline is subsequently distilled; and the gum content, as determined by the more tolerant glass dish method,²⁷⁴ will range from 25 to 60 mg. per 100 cc. For a cracked gaso-

line from an asphalt-base oil, a treatment with 5 pounds of 80 to 95 per cent acid, alkali neutralization, and steam distillation will give much better results than 10 pounds each of acid and contact clay without subsequent steam distillation. The light acid treatment and steam distillation give the gasoline a more stable color, reduce the sulfur by 15 to 25 per cent, and yield a gasoline with only 1 to 5 mg. of gum per 100 cc., as tested by the glass dish method.

Table 53 shows the action of aluminum oxide (similar to bauxite), fuller's earth, silica gel, and sulfuric acid on naphtha having in solution elemental sulfur and sulfur compounds.²⁹⁷ In the experiments, 28 pounds of the adsorbent material was used per barrel (42 gallons) of the naphtha solutions. In the last three columns of the table is shown for comparison the effect of sulfuric acid of different concentrations on the same naphtha solutions. The samples of naphtha solutions treated with the acid were washed with one per cent caustic soda solution after the acid sludge was withdrawn, but they were not redistilled. The amount of acid used was 50 pounds per barrel of naphtha solution.

Table 53. Effect of Adsorbents and of Sulfuric Acid on Naphtha Solutions of Sulfur and Sulfur Compounds.

Stock Naphtha Solution		Adsorbents 28 Lb. per Bbl. Naphtha Solution			Sulfuric Acid 50 Lb. per Bbl. Naphtha Solution		
		Aluminum Oxide	Fuller's Earth	Silica Gel	Fuming	66° Bé.	53° Bé.
Sulfur Constituent	S (%)	Sulfur in Naphtha after Treatment (%)					
Free sulfur	0.26	0.25	0.25	0.24	0.26	0.26	0.26
Isoamyl mercaptan	0.29	0.24	0.28	0.09	0.00	0.22	0.28
Hydrogen sulfide	0.034	0.03	0.03	0.03	0.03	0.03	...
Dimethyl sulfate	0.04	0.03	0.00	0.00	0.00	0.00	0.01
Methyl- <i>p</i> -toluene- sulfonate	0.15	0.15	0.05	0.03	0.00	0.035	0.15
Carbon disulfide	0.08	0.08	0.08	0.08	0.08	0.08	0.08
<i>n</i> -Butyl sulfide	0.30	0.30	0.29	0.13	0.00	0.02	0.29
<i>n</i> -Propyl disulfide	0.38	0.36	0.32	0.24	0.00	0.16	0.35
Thiophene	0.09	0.09	0.08	0.08	0.00	0.01	0.08
Diphenyl sulfoxide	0.05	0.05	0.00	0.00	0.00	0.005	0.01
<i>n</i> -Butyl sulfone	0.08	0.07	0.00	0.00	0.00	0.00	0.01

The data show that silica gel is a little more effective desulfurizing agent than fuller's earth or aluminum oxide, but all three are much less effective than sulfuric acid.

Borgstrom and co-workers²⁸ find that pentamethylene sulfide is removed to some extent by silica gel.

The method of preparing silica gel affects its power for desulfurizing oils. Woodward²⁹⁸ found that a commercial grade of gel removed 18 per cent of the total sulfur from a naphtha solution of crude oil from Ingle-

wood, California, whereas a Holmes gel removed 37 per cent of the sulfur; the adsorbent was equal to the weight of the oil in both cases. Almost all the sulfur compounds adsorbed can be fractionally extracted from the gel by using in turn naphtha, benzene, and ether. Sodium hydroxide solution liberates the remainder. Because different grades of silica gel and different stocks are used, the experimental results of different investigators do not always agree. Thus an appreciable portion of isoamyl mercaptan was shown in Table 53 to be removed by a large amount of silica gel; another research showed that 0.03 per cent of the total ethyl mercaptan content of a gasoline solution was adsorbed by wet silica gel, and 0.07 per cent to 0.12 per cent when dry silica gel was used. The increase in moisture content of silica gel from 6 to 10 per cent practically destroys its adsorptive power for sulfur compounds. The effect of the size of grains of the gel on its adsorption of sulfur compounds is rather small.²⁸⁴

Table 54 gives the results of another investigation on the removal of certain added sulfur compounds from an otherwise sulfur-free kerosene by means of a comparatively large amount of silica gel (56 to 87 pounds per barrel).²⁸³

Table 54. Effect of Silica Gel on the Extraction of Sulfur Compounds from Kerosene.

Sulfur Compound	Solution Used (cc.)	Silica Gel Used (grams)	Sulfur (%)		Decrease (%)
			Before	After	
$(C_2H_5)_2S$	100	25	2.83	1.91	33
C_6H_5HS	150	25	0.93	0.64	31
C_6H_5CNS	125	20	0.46	0.06	88
C_6H_5NCS	125	25	0.465	0.39	17
$(C_2H_5)_2SO_4$	150	25	0.465	0.00	100

The data of Table 55 were obtained by treating a kerosene solution of various sulfur compounds with 20 per cent by weight of silica gel for 6 hours at 88-90° F.²⁸⁵

Table 55. Silica Gel and Sulfur Compounds in Kerosene.

Compound	Original Concentration of Sulfur (%)	Sulfur Actually Removed (%)
$(C_6H_5)_2S$	1.012	0.138
$(C_6H_5CH_2)_2S$	1.117	0.300
$C_6H_5CH_2SH$	0.794	0.225
Elemental S	Not removed.	

These two tables show that only a few sulfur compounds are removed to any great extent from the oil. There are claims, however, that oils can be desulfurized with silica gel; but desulfurization with economical amounts of the adsorbent is obviously impossible, and refiners have very generally rejected the method.

Aluminum oxide, activated by ignition at 650-750° F., is said to adsorb sulfur compounds, especially those in which sulfur is present in an oxidized form. It is suggested that the sulfur compounds be oxidized in the oil before treatment with this adsorbent,¹² an operation obviously impractical for cracked naphthas.

The treatment of oils with air charged with chlorine, or with oxides of chlorine, followed by treatment with bauxite is also patented for removing sulfur,¹⁶¹ but it is certain that the chlorination products left in the oil would be less desirable than the original sulfur compounds.

The following are the results of other tests on the desulfurization of various oils with adsorbents.

When an exorbitant amount of silica gel, 54 per cent by weight of the oil, was applied in two stages to a sample of Mexican kerosene, it removed only 20 per cent of the sulfur from the oil; when the amount of the silica gel was increased to 117 per cent by weight of the oil, it removed only 60 to 70 per cent of the sulfur.²⁸² Another investigation showed that a large amount of silica gel decreased the sulfur content of various oils only 20 to 50 per cent.²⁸³

Treatment of kerosene by the Burmah Oil Company with 80 to 360 pounds per barrel of hot granular bauxite reduced the sulfur from 0.134 per cent to 0.02 per cent. When the same amount of bauxite was applied cold, the sulfur content was decreased only to 0.11 per cent. For the sulfur reduction, it is emphasized that the bauxite must be dry.⁶³

The percolation of oils through fuller's earth removes some of the sulfur compounds. For example, the sulfur content of a California oil was 0.541 per cent; after percolation through fuller's earth, the sulfur content of the consecutive fractions from the filter was 0.11, 0.144, 0.179, and 0.29 per cent. The number of pounds per barrel of oil was not calculated.⁹¹

All these results show that only under exceptional circumstances, if at all, could the sulfur compounds be removed commercially from oils by means of adsorbents, because of the prohibitive amounts. The recommendation of Dunstan and Thole⁶⁴ for the use of as much as 160 pounds of floridin or of 360 pounds of bauxite per barrel of gasoline can be taken as representing the proportions necessary for desulfurizing the average gasoline.

Investigations show that as a general rule adsorbents in economic proportions have little value for deodorizing petroleum products. However, in preparing certain special products, for which the quantity of adsorbents used is of less importance, the adsorbents may be used as the final step for removing traces of odor. Adsorbents are also used to remove the taste and odor from waxes used in the preparation of food wrappers and for similar purposes. It is claimed that for these uses, bauxite, particularly fresh, may have some economical advantages over regular fuller's earth.

Adsorption of Nitrogen Compounds

Nitrogen compounds are removed to a certain extent from the oil by various adsorbents.⁷¹ For example, when a California crude oil of 0.761 per cent nitrogen content was filtered through fuller's earth, the nitrogen in the successive fractions of the filtrate was 0.08, 0.116, 0.289, 0.315, and 0.332 per cent, respectively; the oil retained by the earth contained 0.205 per cent of nitrogen in the upper section of the column, 0.43 per cent in the middle section, and 0.94 per cent in the lower section.⁹¹

Nitrogen bases readily form salts with sulfuric acid; when a light oil, such as gasoline or kerosene, is acidified with a little of the acid (0.1 to 0.5 pound per barrel) and then treated with finely powdered contact adsorbents and filtered, these salts are removed from the oil. The bases can later be released from the acid and clay by adding caustic soda, which neutralizes the acid and frees the bases. Even when the adsorbents are moistened with water, these salts are appreciably hydrolyzed, as indicated by the odor characteristic of the pyridine and quinoline bases.

Adsorption of Oxygenated Compounds

Oxygenated compounds often adhere to adsorbents. Naphthenic acids belong to this class of compounds, although they cannot be thus removed economically. Acids of high molecular weight appear to be more readily adsorbed than those of low molecular weight, but this greater apparent adsorption applies to total weight and not to actual mols of the organic acid.¹⁰¹ Only a few, if any, of the adsorbents can completely remove the organic acids from lubricating oils; this use of the adsorbents is seldom attempted in practice since the large quantity required is uneconomical. For instance, the treatment of an oil with 10 per cent of Florida earth reduced the neutralization number to only 0.4-0.8;²⁶⁹ the neutralization numbers of high-grade lubricating oils seldom exceed 0.01-0.02.

Adsorbents remove strong acidic substances, such as sulfuric acid and sulfonic acids, from oils.

Koetschau¹⁵² reports that silica gel in combination with a small quantity of sulfuric acid is much more efficient in removing organic acidity than silica gel alone.

The subject of removing organic acids from lubricating oils by means of adsorbents is discussed later under the subject of refining lubricating oils and other heavy petroleum products.

Aldehydes and alcohols are also removed from petroleum products by different adsorbents; and it is well known that the decolorizing power of clays for oils decreases in the presence of the more polar compounds, such as alcohol, acetone, etc., as the polar compounds are adsorbed first.²⁵⁹

Some of the gum-forming constituents of light oils are removed by

passing the oil vapors through a bed of fuller's earth or other similar material. On the other hand, when cracked distillates are treated with adsorbents in the liquid phase without redistillation, their gum content is usually not materially decreased; they contain in solution the polymerization products catalyzed by the clay.

Evers and Schmidt ⁷⁵ show that the rate of oxidation of oils is increased by dispersing the oil on silica gel impregnated with an oxide catalyst; vanadium, molybdenum, or tungsten oxides in combination with ferric oxide are the most active oxidation catalysts. This property is said to possess value for the artificial aging of oils.

METHODS OF APPLYING ADSORBENTS

Adsorbents are generally used in connection with chemical reagents in refining; in only a few isolated cases, as in treating some of the Pennsylvania heavy distillates and residual oils, is the adsorbent the only refining agent used. In liquid-phase refining, light oils, such as gasoline and kerosene, are usually treated first with acid and then with the pulverized adsorbent while the oil is still in the acid state, but after the acid sludge is settled out. The discovery was made long ago that these oils are decolorized by an adsorbent more efficiently in the acid than in the alkaline or neutral state.^{204, 205}

When lubricating oils are decolorized by percolation through granular earths, the acid oil is generally first neutralized and thoroughly washed with water. However, in the "dry neutralization" and bleaching of acid-treated lubricating oils (acid oils) by means of contact clay, the powdered clay and the oil are heated together from 250 to as high as about 700° F., cooled to a practical filtering temperature, and filtered. The time of contact between the oil and clay at the highest temperatures is very short, one to ten minutes, but at lower temperatures a longer time is necessary.

In certain cases, a light oil may be treated with the adsorbent after the oil is treated with acid and washed with water or alkalis, but without reacidification. In this method adsorbents are used primarily for the complete removal of the alkalis and soaps, which remain in the acid-treated and neutralized oil, and for the stabilization of the color.

Immediately after a laboratory treatment of a light petroleum distillate with sulfuric acid and alkali solution, a little clay can be added to adsorb completely the water, salt, and excess alkali. The oil can then be filtered, and the tedious process of washing with water to neutrality avoided. One gram of clay retains about 0.6 gram of watery solution, and a small amount of wet clay has no immediately measurable effect on the properties of the light oil. If the light oil is treated in the acid state with clay, washing with alkalis can usually be avoided, although if a very strong

acid and a limited amount of clay are used, it may be desirable to wash the oil with an alkali solution to remove all traces of sulfur dioxide in order to secure stability of color.

A light oil may be acidified with hydrochloric acid instead of sulfuric acid before the application of earths for color improvement, but the economy is not apparent. The use of sulfur dioxide for the same purpose is patented;¹⁶⁷ but as the sulfur dioxide is not adsorbed by a normal amount of clay, a subsequent wash with caustic soda is imperative or the color will revert.

REFINING BY PERCOLATION

The percolation method of refining with adsorbents is usually applied to lubricating oils and waxes, sometimes to kerosenes, and very rarely to gasolines.²⁵² The percolation process requires more of the granular absorbent per unit of oil than the "contact" process requires of the powdered earth, but the granular clay readily lends itself to repeated revivification, whereas the powdered clay cannot be so revived. The relative costs of decolorizing a lubricating oil by percolation and by contact methods are shown on pages 290 and 291. However, not all the properties of the oil are affected equally by the percolation and contact processes. This difference is explained by the fact that percolation is to a certain extent comparable to a countercurrent method of applying the adsorbent, whereas the contact process is, within certain limits, a batch or equilibrium process.¹³⁸

The plant percolation filters may be of any general size, but they are usually cylindrical, 6 to 10 feet in diameter, and 14 to 30 feet high.⁹⁷ Their capacities vary from 10 to 60 tons of clay, or double that for bauxite, the apparent density of which is about double that of fuller's earth. The shape of the percolators is, in general, of little importance, provided it is not conducive to channeling. The percolators are filled with the adsorbent material except for free spaces of 1 to 2 feet at the top and at the bottom. The adsorbent is supported by a perforated plate at the bottom; in antigravity filtration a similar, but inverted, arrangement is provided at the top. Suitable openings at the top and at the side near the bottom of the percolator are provided for charging and discharging the adsorbent. It is generally recommended that the percolators be insulated and that the temperature of the clay and the oil remain uniform through the run, a procedure not always followed.

Details of filter construction are given by Kauffman.^{141, 143} He particularly recommends filters 7 feet in diameter and 22 feet high for the percolation of lubricating oils. Structural features of the percolation filters are also detailed in a number of patents, such as those issued to Clark and Warren,⁴⁰ Payne,²⁰⁰ Naef,¹⁵⁵ etc.

It is preferable to charge the filters with clay directly from the kilns, or at least as soon as possible after the clay is burned, in order to keep

the clay as free as possible from excess moisture and to help maintain the desired temperature in the filters. After the clay is charged, the oil is pumped to the top or to the bottom of the filter, the procedure depending upon whether gravity or antigravity filtration is used. The latter is preferable because it lessens channeling. Antigravity percolation of such products as medicinal oils,¹⁰⁴ cracked gasoline,²²¹ and special types of oils, like transformer oils,¹⁴³ has been patented. The use of antigravity filtration requires somewhat reinforced filters, as greater pressure must be applied.

In charging the percolator columns the oil and the clay are sometimes introduced simultaneously by pumping in order to insure freedom from air-pockets and to decrease the soaking time. The filter is then allowed to "soak," *i.e.*, the oil is permitted to percolate through the column of clay. When it becomes filled with oil, the filter may be shut off for a few hours to provide thorough contact between the clay and the oil. This additional soaking time is generally unnecessary unless the oil is very thin and tends to flow too rapidly.

Percolation of the oil through the tower is continued until the blend of the percolated oil in the run-down tank, and not the oil then leaving the percolator, has sufficiently good color to meet specifications. However, it may be advantageous to prolong the percolation until the color of the oil leaving the filter is practically as dark as the charging stock. The darker oil is segregated in separate tanks and later re-percolated through a new charge of clay.

After the clay in the tower is exhausted, the filter is drained, and as much of the oil as possible is recovered. The filter is then washed with naphtha, usually 58° A. P. I. or lighter, and steamed at a pressure of about 45 pounds per square inch if the filters are sufficiently strong to withstand this pressure. The steaming is usually continued until oil is no longer seen in the steam condensate. The pressure is then released, and the clay removed and ignited at about 1100° F., cooled, and returned to the filter or stored for later use. Before the ignition the total quantity of carbonaceous material, including the impurities, is usually not over 5 or 6 per cent by weight of clay, and the oil is not over 1 per cent by weight of the clay.

Ridgway, Henderson, and Ross²²⁴ have made an extensive investigation of the recovery of oil from spent percolation filters. The study was limited to fuller's earth and to Pennsylvania oils which had not been acid-treated or solvent-extracted.

The original publication of Ridgway and associates should be consulted by those interested in the percolations. Among their observations only the following are noted here. The rate of draining and the total amount of the oil drained from the filter depend primarily on the conditions of the filter.

A naphtha that is highly paraffinic in nature and of low vapor pressure and low end boiling point should be used in washing the oil from the filter. The naphtha should be applied to the filter at a low, uniform rate, first at a temperature below that of the filter to recover the filterable oil, and then at a temperature above that of the filter to dissolve the adsorbed organic material, or tar. Much of the oil extracted from the filter is "filterable," that is, it is suitable for returning to the percolator for bleaching, but the remainder is not. The color of the extracted oil is not a criterion of its fitness for refiltering; its suitability can be determined by experiment only.

Not all adsorbents retain with equal tenacity the impurities extracted from the oil. Bauxite, for example, releases the coloring matter when washed with naphtha much more readily than fuller's earth; for this reason care is needed to avoid over-washing the bauxite filters during the oil extraction process.

The heavy residual stocks are often dissolved in light solvent and then filtered. The disadvantages, as well as the advantages, of diluting oils with naphtha, which were discussed in connection with refining with sulfuric acid, pertain to a large extent to percolation processes. Some of the oils are injured by the high temperatures required to expel the naphtha.

Oils diluted with naphtha can be filtered at lower temperatures than the undiluted stocks because of their lower viscosity. However, the proper temperature for percolating the diluted oils is as important as that for the undiluted oils. In many cases, temperatures higher than those required to obtain the desired filtering rate may be desirable.

Hubbell of the Attapulugus Clay Company has investigated the type of solvents for use in dissolving oils that are to be percolated, and the degree of the dilution. The following data are published with his permission.

The results of Hubbell's work show that an increase in the paraffinicity of the solvent results in an increase in the yields of decolorized oil from both fuller's earth and bauxite, the influence of the solvent paraffinicity being more pronounced at lighter finished-oil colors (5 A. S. T. M.) with bauxite, and at darker colors (8 A. S. T. M.) with fuller's earth. An increase in paraffinicity of the solvent was also found to result in an increase in the so-called "solvent refining" action of both bauxite and fuller's earth, as evidenced by a somewhat higher A. P. I. gravity, lower viscosity, lower carbon residue, and a changed cast of the finished oil. For a solvent of a given paraffinicity, an increase or elevation in boiling range results in decreased yields of decolorized oil with either fuller's earth or bauxite; however, with bauxite this trend toward lower yields caused by the use of a heavier solvent may be offset by the fact that advantage may be taken of the higher filtering temperatures made possible by its lower

Table 56. Solution Percolation of Pennsylvania Cylinder Stock. Effect of Solvent Characteristics and Dilution.

Subject Adsorbent	Effect of Boiling Range and Paraffinicity										Effect of Dilution ¹	
	Attapulgus 30/60 Mesh Bauxite (3)					Attapulgus 30/60 Mesh Clay (3)					Attapulgus Bauxite	Attapulgus Clay
	Paraffinic		Aromatic			Paraffinic		Aromatic			Paraffinic	
	53.9	54.7	Below 0	Below 0	Below 0	53.9	54.7	Below 0	Below 0	Below 0	53.9	53.9
Aniline Point of Solvent (°C.)	176	304	206	276	276	176	304	206	276	276	176	176
Initial Boiling Point (°F.)	216	306	306	330	306	216	330	227	306	306	216	216
50% Point (°F.)	297	385	276	347	276	297	385	276	347	297	297	297
End Point (°F.)	+30	+30	+30	+26	+26	+30	+30	+30	+30	+26	+30	+30
Solvent Color (Saybolt)												
Percolation Tests (1)												
Solution Per Naphtha	60	60	60	60	60	60	60	60	60	60	70	70
Percolation Temp. (°F.)	135	135	135	135	200	135	135	135	135	200	135	135
Filter Yield—Bbbls./Ton												
5 ASTM Oil Color	5.3	3.9	2.1	1.4	0.7	7.4	5.6	4.5	3.2	1.7	5.3	7.4
6 ASTM Oil Color	6.1	3.2	3.4	2.5	1.6	9.2	7.6	6.4	4.8	2.9	5.6	9.4
7 ASTM Oil Color	6.9	6.5	4.8	3.8	3.0	11.4	10.2	8.5	6.7	4.5	6.1	7.0
8 ASTM Oil Color	7.8	7.8	7.0	5.8	4.9	14.3	13.9	11.0	9.5	7.1	7.9	11.8
Bauxite Efficiency (Vol. Basis)											8.7	14.3
5 ASTM Oil Color (2)	126.5%	123%	82.5%	77%	138.5%	...
6 ASTM Oil Color	117	120.5	93.8	92.3	131.5	...
7 ASTM Oil Color	107	112.5	100	100	118.5	...
8 ASTM Oil Color	96.2	99.0	112.5	108	107.5	...
Finished Oil Inspections (Undewaxed—8 ASTM)												
Gravity	28.2	...	27.8	27.7	...	27.4	28.3	27.5
Viscosity at 210° F.	134	...	139	142	...	146	134	143
Conradson Carbon	.8398	1.41	...	1.4988	1.38
Cast	Poor+	...	Fair+	Good	...	Good	Poor+	Good

- (1) Stock used—Pennsylvania "A" Cylinder Stock of 5650 O.D. Color, 2.23 Carbon, 155 Vis., at 210.
 (2) Efficiencies based on corresponding yields from fuller's earth using density ratio of 54.5:30.9.
 (3) All tests by Attapulgus Standard Methods; Bauxite burned at 1200° F., fuller's earth at 900° F.

volatility. The percentage of diluent in the solvent-oil blend also has an effect upon the yield of oil which may be decolorized with bauxite. It was found that increasing the percentage of the diluent from 50 per cent to 70 per cent gave 35 per cent increase in the yield of oil to a given color with bauxite. With fuller's earth, however, the oil yield did not vary appreciably within this range of dilution. Dilutions with less than 50 per cent solvent showed decreasing yields with fuller's earth; however, it was noted that fuller's earth was much less sensitive to this effect than bauxite.

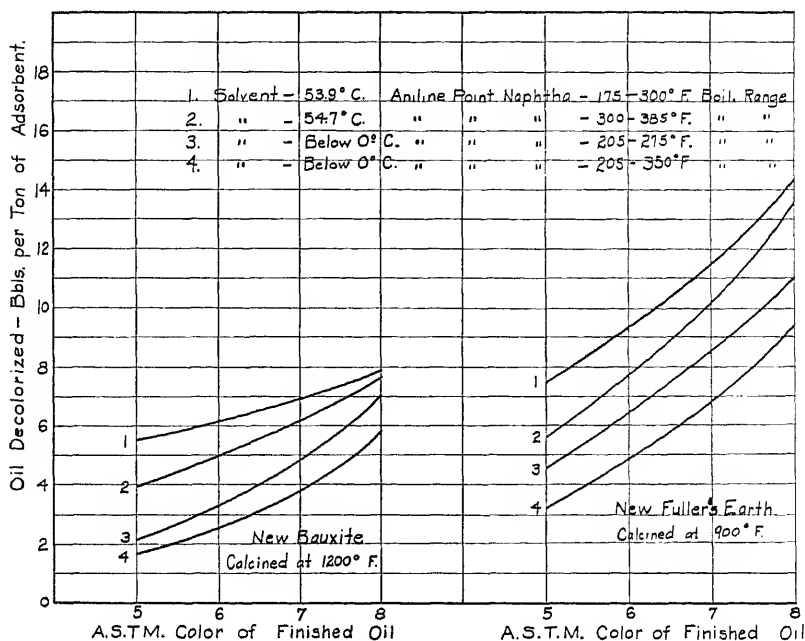


FIGURE 15. Effect of Paraffinicity and Boiling Range of Solvent in Solution Percolation of Pennsylvania Cylinder Stock (60% Solvent, 40% Cylinder Stock; Filtering Temperature, 135° F.).

The results of this investigation are presented in Table 56 and Figures 15 and 16.

Various modifications of the percolation procedures are in use. For instance, an oil of low or medium viscosity and bearing an appreciable quantity of wax may or may not be treated with sulfuric acid and neutralized with caustic solution before percolation. The lighter lubricating oils may be passed without dilution through the percolator at a predetermined optimum temperature and rate; but often the more viscous oils are first diluted with enough naphtha to provide sufficient fluidity for intimate con-

tact with the adsorbent. After percolation through the granular earth the light, undiluted lubricating oil may be diluted for the first time, and the heavy, diluted oil may be still further diluted with naphtha for dewaxing; then, after the oils are dewaxed, the naphtha is expelled.

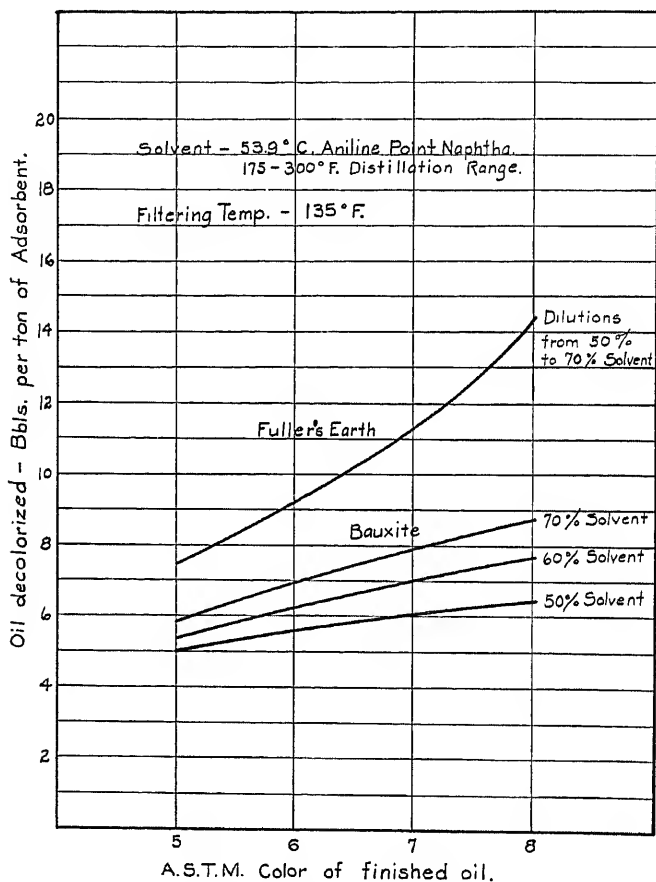


FIGURE 16. Effect of Degree of Dilution in Solution Percolation of Pennsylvania Cylinder Stock.

When the lubricating oil is diluted with naphtha before percolation, less oil is left on the adsorbent. The naphtha is less expensive than the lubricating oil, and its loss is less serious. Nevertheless, the loss of naphtha in blends with oils in the percolation process is appreciable: in extreme, though rare, cases it may be 2 per cent in blending, 3 per cent in filtering, 2 per cent in heating for centrifuging, 3 per cent in the distillation, and 3 per cent in washing the percolators.³¹

Kauffman¹⁴³ has developed data on the refining of a steam cylinder oil by diluting it with naphtha, percolating it through granular fuller's earth, and then distilling out the naphtha and bringing the oil to the desired flash and fire points. These data are presented in Table 57. The first oil coming through the filter shows very marked differences from the original oil in temperature, gravity, sulfur content, pour point, iodine number, and carbon residue, but the last oil coming through the filter shows but little change. The total amount of oil passed through the percolator is determined by the quality desired in a composite sample of the filtered oil. The lack of uniformity in the successive portions of the percolated oil is one of the reasons for the rapid development of the newer contact processes, in which all portions of the oil are equally refined.

Table 57. Changes in Successive Portions of Heavy Lubricating Oil from a Percolating Tower.

	Original Stock	First Through Clay	10 Bbl.	23 Bbl.	75 Bbl.	148.4 Bbl.	294.6 Bbl.	500.4 Bbl.	589.4 Bbl.
Temperature of filter stream, (° F.)	...	106	136	118	106	84	68	68	68
Gravity (Bé.)	41.6	49.0	48.3	46.2	43.2	42.4	41.9	41.8	41.5
Sulfur (%)	0.134	0.011	0.020	0.045	0.080	0.128	0.125	0.133	0.129
After Reducing									
Gravity (Bé.)	23.0	30.7	29.7	27.7	25.4	23.9	24.1	22.9	23.3
Flash (° F.)	430	460	480	440	420	435	470	440	440
Fire (° F.)	540	535	540	540	535	540	545	540	535
Vis., 100° F.	3122	819	892	1148	1937	2291	2662	2722	2798
Vis., 210° F.	156	90	87	95	125	135	140	140	140
Pour (° F.)	60	55	55	55	65	65	65	65	65
Iodine value	18.0	0.61	1.2	4.3	12.1	14.8	16.4	17.4	18.1
A.S.T.M. carbon residue (%)	2.25	0.008	0.027	0.115	0.546	0.932	1.49	1.61	1.79

The temperature is important in percolation processes and is determined experimentally for each stock. For lubricating oils and cylinder stocks, it is usually 120 to 130° F., but occasionally is as high as 225° F.; for other oils it is not over 90 to 100° F.; for waxes and petrolatum it is usually about 25° F. above their melting points. Too high temperatures are to be avoided. If the oil is too hot, it should be cooled before it is filtered;³¹ otherwise, the color may be impaired. However, too low temperatures are also to be avoided, as then the clay is not so efficient in its decolorization.

Lubricating oils are practically always supplied to the percolators in a neutral condition whether or not they have been treated with acid. Some use is made of the percolation methods in small refineries for improving the color of straight-run gasoline and kerosene after acid treatment and neutralization, but this practice is limited; the operation is conducted at normal temperatures.

It has been reported that, in the desulfurization of kerosene, alternate cold and hot filtrations through bauxite give better results than either one

separately.⁹⁷ However, such a procedure for desulfurization of kerosene would be impractical and far more expensive than the use of sulfuric acid or liquid sulfur dioxide.

The use of different adsorbents in series has also been considered at various times, but the process appears somewhat complicated for refinery use.

Adsorbents Used in Percolation

Fuller's earth and bauxite are nearly always used as adsorbents in refining by percolation, although charcoal,¹⁰² bog iron ore,²⁹² and other adsorbents have been patented for this purpose. The proper mesh of the adsorbent is important for economy and for obtaining the best results. It is reported that for equal weights, an earth of 60/90 mesh has an efficiency of about 10 to 15 per cent greater than one of 30/60 mesh, and the latter about 20 per cent greater than one of 16/30 mesh.³¹ A material of 20/90 mesh is, however, very frequently used in practice, as with it less channeling occurs. For viscous distillates, 16/30 mesh earth is often used. The lower-viscosity oils permit the use of more finely divided adsorbents in the percolator than do the heavier oils. In actual commercial operation the refinery, as a rule, selects the proper mesh of adsorbent which satisfies its most important needs and applies the same adsorbent to other oils as well; otherwise a large number of clays would have to be segregated.

A British patent specifies mixing different adsorbents, *e.g.*, mixing bauxite with 20 to 30 per cent of floridin. With this modification, the floridin presumably adsorbs primarily the color-forming substances, and the bauxite the sulfur compounds.⁶² A mixture of 75 per cent bauxite, 5 per cent bentonite, and 20 per cent starch, which has been heated to at least 1300° F. and cooled, is also recommended;¹⁹⁴ this mixture is recommended primarily for vegetable oils.

An interesting study of adsorbents with particular relation to bauxite as a refining agent for crude petroleum and their by-products has been made by Guiselin of the Anglo-Persian Company.⁹⁷ He presents theories of the decolorizing and desulfurizing action of these materials, as well as the practical methods of using them and of testing their efficiencies, the type of filters and of agitation, the factors involved in revivification, etc.

Hubbell and Ferguson¹²⁵ report their recent studies of bauxite for percolating lubricating oils. The original articles should be reviewed by those interested, for only a few of their conclusions can be noted here. They find that in the percolation of residual stocks dissolved in solvents bauxite retains throughout its life approximately 85 per cent of its initial efficiency, whereas in the straight percolation of bright stocks it retains about 80 per cent. They also find that the bauxite used to filter distillate stocks requires low

temperatures for its revivification; therefore, the bauxite used on residual stocks should be segregated from that used on distillate stocks. Under optimum conditions the efficiency of bauxite used in percolation of Pennsylvania "neutrals" may be maintained at 55-60 per cent. They point out that bauxite is superior to other adsorbents for the percolation of petrolatums and related stocks because it gives high yields and tasteless and odorless products.

CONTACT FILTRATION

Many petroleum products are treated by the contact process; different refineries use various modifications in the general method of procedure.¹⁷⁹

For early bibliography, see Francis⁸² and Typke⁷⁰ and the early patent literature.⁶

The clay is most frequently ground to 200 mesh, although 100-mesh or 325-mesh clay is also used. If very fine adsorbents are used, filter-aids, such as the infusorial earths, may be added.

The oil is preferably, but not necessarily, first treated with sulfuric acid and then brought into contact with the finely divided adsorbent while in the acid state.⁵⁹ The contact treatment of straight-run gasoline, and to some extent kerosene, in the acid state is common practice. Lubricating oil may be in an acid, neutral, or, in very special cases for removing the organic acids, in a slightly alkaline condition.

Straight-run gasoline and kerosene stocks are always treated at normal temperatures in the contact process. However, the temperature of treatment of the lubricating oils and the contact adsorbent is from 250 to 350° F., or for especially heavy oils from 600 to 700° F., or even to the initial cracking temperature of the oil, as in the preparation of steam cylinder oil from Pennsylvania residual stocks.

The oil and adsorbent are thoroughly mixed; and if high-temperature contacting is used, as with lubricating oils, the mixture is heated by pumping it through a tubular furnace. Agitation is as a general rule mechanical, although for certain products, such as kerosene, air-blowing may be satisfactory. The spent clay is then separated from the oil, either by filtering the oil through sand or other types of filters, by centrifuging, by direct settling in the treating tanks, or by continuously settling in a tank and filtering or clarifying the oil overflowing from the tank. Continuous treatment is used almost exclusively.

If cracked gasoline is to be treated with clay after the acid treatment, it is usually desirable for the stability of color to remove most of the acid sludge immediately (2 minutes or less) after agitating the oil and acid. The sludge can be separated by one of the methods described under

refining with sulfuric acid, such as by centrifuging, passing through coarse gravel (a modified capillary separator), or otherwise.

For description of contact plants, see Kauffman (Producers and Refiners Company Plant, Parco, Wyoming);¹¹² Truesdell (Solar Refining Co., Lima, Ohio);²⁰⁸ Wadsworth (Independent Oil and Gas Co., Oklahoma);²⁷⁰ Clark and Gundelfinger (Marine Refining Co., Vernon, California);¹⁵ Reid (gasoline treatment at Marine Oil Corporation);²¹⁵ Reid (Deepwater Oil Refineries Co., Houston, Texas);²¹⁰ Reid (long residuum treatment at a Pennsylvania refinery);²¹⁷ Harris (Wait Process);¹¹⁰ etc. Apparatus suitable for treating oils with clays are specified by Prutzman,²⁰⁹ Bollman,²⁷ Benjamin,¹⁰ Bell,¹⁹ Black,²³ Carpenter and Moorman,³⁵ Hindelang,¹¹⁵ and many others.

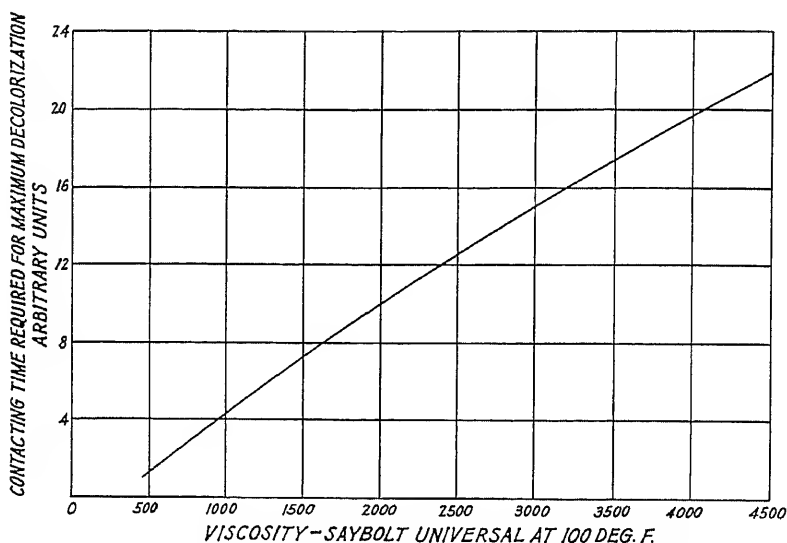


FIGURE 17. Relationship between Oil Viscosity and Time Required for Maximum Decolorization at Fixed Temperature.

The time of contact between a light oil and the adsorbent is usually short, from one to several minutes. It may be longer with heavier oils and may be as long as 45 minutes for certain types of German clays.⁶⁶ It is stated that in treatments with decolorizing carbon, the time of contact may be extended to 24 hours.²²³ An empirical relationship between oil viscosity and the time required for maximum decolorization at fixed temperature and rate has been developed by Funsten⁸⁶ and is shown in Figure 17.

The method designed by the Raffineries de Pétrole de la Gironde, Bordeaux, France, for decolorizing by continuous operation 10,000 barrels of cracked gasoline daily may be of interest, especially because of the short time of contact between the sulfuric acid and the gasoline.²⁶⁵ The acid

(0.8 pound of 66° Bé per barrel) is mixed with the oil by three mechanical mixers in parallel; after only three seconds of contact, the acid sludge is separated by means of a battery of 15 centrifuges in parallel; the slightly acidic gasoline is commingled with clay of 200 to 300 mesh; and in about four minutes the clay is separated by two Sweetland filters. It is pointed out that the three seconds of contact between the acid and cracked naphtha produces so little polymerization that the end boiling point of the gasoline is not raised, and the acid itself contains only about 26 per cent of oil by weight (oil, 9° Bé), whereas on long contact the sludge would have contained 67 per cent of 28° Bé oil. The color of the finished gasoline is 28 to 30 Saybolt and is said to be stable. No data are given on the gum content.

The methods of treatment of oils by contact vary. A common practice of treating by contact is that of adding the adsorbent to the oil, agitating, and then filtering the oil through a bed of adsorbent; this method unites the principles of contact and percolation processes.¹⁷² In another very old modification, clay is added to the oil in the still, and the oil distilled. Recently this method has been revived in refining lubricating oils; it is known as Filtrol Fractionation, under which name it will be described later.

Contact Decolorization of Light Oils

Light distillates, such as straight-run gasoline and kerosene, can be brought into contact with clay either after settling and withdrawing the main portion of the acid sludge subsequent to acid treating,²³³ or without withdrawing the sludge.²⁰⁵ Both of these methods are commercially successful, but generally it is preferable to separate the greater portion of the acid sludge before adding the clay. If the sludge is not withdrawn, all the sludge produced on contacting the oil with the acid is adsorbed by the clay. The latter, or Pollock, process is, however, used only when comparatively small amounts of acid are used, usually much less than one pound per barrel. As a limited quantity of acid, about 60 per cent by weight, can be adsorbed by the clay, the ratio of acid to clay cannot exceed this amount without leaving acid in the oil.

The ratio of acid to clay for best decolorization varies with the type of distillates; with some distillates an acid-clay ratio of 0.6:1.0 gives best results, with others a ratio of not over 0.1:1.0 is best. Pinkish coloration of the treated gasoline is an indication that excess acid has been used. A small quantity of acid is necessary with an unactivated clay for increasing the decolorizing action of the clay; and when large amounts of clay are used in treatments, part of the acid may be left in the oil or a small amount of fresh acid added before the clay is introduced. Sometimes the acid and clay can be added to the oil simultaneously, or the acid and clay can

be mixed first and then applied to a stock or neutral oil. These two methods are less satisfactory than preliminary addition of the acid.¹⁴⁴

The strength of sulfuric acid used to acidify the oil may vary within rather wide limits. For color reduction of straight-run gasoline, acid of 95 to 96 per cent concentration is most efficient, although 93 per cent acid is used almost exclusively for the reasons explained in the discussion of sulfuric acid treatment. Acid of 65 to 80 per cent concentration may in rare cases give better results than 93 per cent acid, especially in treating light oils which have a tendency to develop a pink color.

For producing a more stable color or a better initial color, a caustic wash before the acid-clay treatment of gasoline or kerosene is frequently extremely helpful.^{45, 139} The alkali treatment of lubricating oils after the acid-clay treatment,¹³⁶ or between two acid treatments of any stock,²⁸⁷ often yields better color, even though the operation is difficult to carry out. Water washing before any chemical treatment is often beneficial, especially for cracked products.¹⁸⁴ It is necessary to determine experimentally which of these modifications, if any, improves the decolorization of a given stock.

The clay can be applied in one portion, in several portions,¹⁵⁸ or continuously. In the treatment of light oils with small quantities of clay, the efficiency is not affected whether the clay is added in one or in several portions, and consequently it is added in one portion. Mechanical agitation is preferable to air agitation for mixing the clay with the oil; with air agitation the evaporation of light oils is excessive, the fire hazard is greater, and the air in contact with the clay may in rare cases discolor the oil. The last phenomenon is observed with heavy oils at high contact temperatures.¹⁶⁹

At times air agitation of gasoline or kerosene gives very much better color than mechanical agitation, but a prewash with caustic solution or with water often corrects the deficiency in the mechanical agitation;^{45, 139} however, a caustic wash subsequent to the clay treatment does not improve the poor color resulting from the mechanical agitation. With most kerosene stocks the results from mechanical and air agitation are the same.¹⁵³

The cause of the above sometimes anomalously low efficiency in the mechanical agitation has not been explained, although it is known that the effect is not due to the presence of sulfur dioxide, since actual agitation of the oil and clay by means of a large volume of gaseous sulfur dioxide, followed by separation of the clay and immediate extraction of the sulfur dioxide with alkali solution, gives just as good color as air agitation. It must be noted that the above non-injurious effect of sulfur dioxide on the color of the oil is not to be confused with its effect when left in contact with the oil for several days, a condition under which it has a very

deleterious effect on the color. This reversion in the color of an oil on long contact with sulfur dioxide is assumed by Brooks³² and by Cassar³⁷ to result from the oxidation of the sulfur dioxide to the more reactive sulfuric acid, which attacks the oils and forms sludge.

Other gases—nitrogen, hydrogen, and methane—have been used to agitate kerosene and clay and give as good color as agitation with air.

Fuming acid is frequently used to lower the total sulfur content and to improve the burning quality of kerosene stocks derived from asphalt-base or mixed-base crude oils, but the color may still be dark. An immediate application of contact clay has but little effect on the color, and the oil still reeks of sulfur dioxide. However, if the acid oil is neutralized with caustic soda solution, re-acidified with about one pound of 66° Bé sulfuric acid, and then treated with 2 or 3 pounds of clay, with or without withdrawing the acid, the color will be greatly improved; because of the small amount of acid used, the oil will not again need to be neutralized with caustic soda solution.

Clay is sometimes used primarily for stabilizing the color of a neutral oil after the acid treatment and neutralization with caustic soda solution; but under these conditions the clay is not so effective in removing the existing color, especially from light oils which are treated at normal temperatures. Clay refining of oils which have been neutralized with sodium hydroxide has been recommended both for lubricating oils⁸¹ and for cracked distillates.¹⁸⁴

Table 58. Refining Gyro Process Cracked Gasoline at 600° to 625° F. and 200 to 500 Pounds Pressure with Contact Clay.

	Raw Distillate	Finished Gasoline	Polymers
Per cent	100	92.8	6.11
Gravity	55.3	55.1	18.7
I. B. P. ° F.	90	100	392
10 per cent	148	158	508
20 per cent	182	192	556
30 per cent	212	222	588
40 per cent	248	254	612
50 per cent	284	288	632
60 per cent	308	314	654
70 per cent	348	340	679
80 per cent	374	362	716
90 per cent	400	386	760
Endpoint	424	410	...
Color	...	30	...
Gum	...	0.2 Mg.	...

The Pure Oil Company uses the Osterstrom process¹¹⁷ for refining gasoline from the "Gyro" vapor phase cracking units, and other refineries having these cracking units also use the same process. The process is a combination of liquid and gaseous phase treatment with finely divided

clay. The untreated clay, such as fuller's earth, bentonite, and Death Valley clay, is proportioned into a continuous stream of the cracked liquid, and the mixture pumped under a pressure of 200 to 500 pounds and at a high velocity through a tubular furnace, in which the temperature of the mixture is raised to 600 to 650° F. As the mixture leaves the furnace, the pressure is released and the gasoline flashed from the clay and polymerized products, which are cooled and run to a Sweetland filter press; the clay is separated and discarded, and the polymers are stored for other uses. The gasoline is fractionated in the normal manner and condensed. Holland¹¹⁷ submits Table 58 as typical of yields and the characteristics of the refined gasoline.

Aging of Stock and Treatment with Clay

In rare cases petroleum distillates may be "aged" advantageously before treatment, inasmuch as they usually undergo rather rapid change for a week or two after the distillation.⁶³ In general, however, the application of a relatively large amount of adsorbent to the fresh stock is better practice and gives just as stable a product as first aging the stock and then applying the necessarily heavy treatment, *i.e.*, if the same amount of clay is applied to the fresh stock as would be applied after the stock is aged, the color will be equally stable and the delay of storage before treatment avoided. In making accelerated aging tests by exposing oils to the action of the sun or artificial light, it should be remembered that the action of light is different from the normal aging.¹⁶⁹

Contact Refining of Lubricating Oils and Other Heavy Petroleum Products

Contact refining is now used in treating lubricating oils from all types of crude oils, but formerly it was more commonly used on the oils of California.^{21, 55, 245}

Lubricating oils, vaseline, waxes, and other heavy, petroleum products are almost always treated with acid before treatment with clay; the sludge from the acid treatment is withdrawn, and the oil is commingled, usually in the acid state, with the adsorbent. Heavy stocks can retain considerably more acid in suspension than light stocks, and care is taken that most of the acid is removed from the oil. The neutralization number of the lubricating oil after the acid treatment is frequently an indication of the ease with which the oil can be refined by the clay, provided other conditions, such as the physical characteristics of the oil, are equal. Records of the acidity of the oils from the acid treaters should be kept for use in contact refining.

When used in economical amounts, the clay does not remove all the

weak organic acids from the lubricant; therefore the lubricants may not be satisfactory unless the oil has already been freed of the organic acids. The clay readily removes the strong acids, such as sulfuric and sulfonic acids; in this respect the process is very similar to the acid-clay decolorization of gasoline or kerosene.²⁸⁶

Sometimes the acid oil is neutralized with a slight excess of caustic soda solution, and the washings, containing salts of organic acids, are withdrawn. The slightly alkaline oil is then commingled with the adsorbent; and, when heated, almost all the water is evaporated. Under these conditions the concentrated alkali combines more completely with the organic acids to form soaps, which are fairly well removed by the adsorbent.²⁸⁹ The addition to the acid-treated and neutralized lubricating oil of chemicals capable of combining with the weak organic acids and with the alkaline-earth salts of the oil to form compounds which can be removed by subsequent treatment with adsorbents appears to be promising. Thus, a small amount of sodium oxalate in a slightly alkaline solution is added to the neutral, acid-refined lubricating oil; the mixture is commingled with clay at an elevated temperature in order to expel the water, and is then filtered. The calcium which may be left in the oil from water washing is removed as calcium oxalate, and the organic acids as anhydrous sodium soaps.¹⁷⁶ The oil treated in this way is free both of organic acidity and of ash-forming constituents.

Excess of a strong alkali lowers the decolorizing efficiency of the clay and the filtering rate of the oil. In general, a neutral or preferably a slightly acidic condition of the lubricating oil and nearly complete freedom from organic acids or their soaps give best results in the contact clay treatment. Some heavy stocks, such as Pennsylvania stocks, are treated satisfactorily with contact adsorbents without the use of acid,¹²¹ but even with them slight acidification improves the decolorizing power of the clay, sometimes more than doubling it, and much less clay is needed to yield a certain color after the acid treatment.

The amount of clay required for decolorizing heavy oils is much larger than for light oils and varies from 2.5 to 12 per cent or even to 25 per cent of the weight of the oil. Because of the quantity of oil adsorbed by the clay and the cost of its recovery, and because of the cost of the clay itself, heavy clay treatments are avoided as far as possible by using sufficient acid in preliminary refining.

Certain clays, such as the bentonites and those of Death Valley, used for treating heavy petroleum products, are often thoroughly moistened, or even converted into a "mud" with an equal or greater weight of water, before they are applied to a lubricating oil prior to heating the mixture.¹⁴⁶ During the contacting, the additional water is converted into steam, which

helps agitation, and the layer of steam at the surface of the oil prevents oxidation of the oil by the air. The clay can be commingled with the oil by mechanical agitation or by agitation with superheated steam.¹⁴⁸ Air agitation is to be avoided, as oxidation discolors the oil.

Because of the beneficial effect of water in contact clays for lubricating oils, refiners sometimes find it economical to use the wet, acid-activated clay, or pulp, from the activation process without first drying it. In the activation process the clay is treated with approximately its own weight of hot dilute sulfuric acid or hydrochloric acid of about 20 per cent strength, washed with water, and settled until the actual acid left is less than one per cent, and the water is two to three times the dry weight of the clay. This pulp can then be added directly to the lubricating oil.

The Texas Pacific Coal and Oil Company²⁶¹ utilizes the dilute sulfuric acid separated by hydrolysis from the refinery acid sludge to activate the clay and then uses the washed clay as a very wet pulp (20 to 25 per cent of actual clay) to treat an acid-treated lubricating oil; the oil, though in an acid condition, is free from "peppery" sludge.

Staley²⁴⁶ describes the contact process of the Bradford Refining Company, Bradford, Pennsylvania, for treating with dry clay a viscous lubricating oil stock of 85 to 90 Saybolt Universal seconds at 210° F. The dry clay (30 to 40 pounds of California untreated clay of 200 mesh per barrel of oil) is introduced mechanically into the oil out of contact with air. The clay and oil are partly mixed in passing through a pump and then are heated to 600-650° F. in a tube still, where further commingling takes place. The mixture is immediately cooled a little in heat interchangers, mixed with an equal volume of naphtha, and filtered through a filter cloth and again through a blotter press to remove the finest clay, which has passed through the cloth in the first filter. More naphtha is added until the lubricant represents about 30 per cent of the solution. The solution is then cooled to -50° F., the crystallized wax removed by centrifuging, and the naphtha expelled from the lubricating oil with steam at about 350° F. The oil is then "brightened" by percolating it through a small quantity of fuller's earth of 15 to 30 mesh; but as the brightening is not a decolorizing process, the consumption of the granular fuller's earth is slight.

Matusевич¹⁷⁴ describes the combined acid and contact refining of a heavy lubricating oil from the residual oil (long residuum) left in the still after distillation of the lighter constituents from crude oil. Laboratory and refinery experiments show that the long residuum requires 7 to 10 per cent of 96 to 98 per cent sulfuric acid, which is applied as a spray during air agitation. An initial temperature of 85 to 95° F. gives the best results. Agitation is continued until the acid sludge begins to form in

large lumps, as determined by observing samples of the oil from the agitator placed on a plate or filter paper. The time of agitation is usually from 20 to 45 minutes. The main portion of the sludge is withdrawn at once, and the remainder is allowed to settle for 15 to 48 hours at a temperature not higher than 120 to 130° F.; a higher temperature injures the color. Attempts to coagulate the sludge with a little water, alkaline solution, or clay proved valueless. After the removal of the sludge, the acid oil is mixed with a very wet, acid-treated clay (one part of clay to three of water) and circulated through a Foster Wheeler pipe still and tank, in which the temperature is brought to 330° F. The clay, equal to 15 to 25 per cent of the weight of the oil, is added in two or more fractions before a temperature of 212° F. is reached, so as to avoid excessive foaming from the evaporation of the water. On a large scale, a total of six to eight hours is required for introducing the clay and developing the optimum temperature in the oil, although the laboratory data show that a contact of 40 minutes gives better results. The clay is separated from the oil by a filtration process; the clay retains approximately its own weight of oil. Table 59 gives the results of the refining of the long residuum described by Matusevich. The process is not modern, but it is described as an illustration of the various methods applicable to the clay contacting.

Table 59. Acid and Contact Treatment of Long Residuum.

98% H ₂ SO ₄ , % by wt. of oil	..	6	9	12	15
Color of acid oil, mm. ^a	..	41	55	70	80
Color after clay treatment, mm. ^a	9.5	50	68	87	91
Sp. gr.	0.9182	0.9055	0.9046	0.9022	0.8997
Flash point		Practically unchanged			
Conradson carbon (%)	3.70	1.68	1.48	1.16	1.07

^a Depth to match an arbitrary color.

According to Petty,²⁰¹ lower temperatures are permissible when the heavy oils are first diluted with naphtha; the low viscosity of the blend aids in securing good contact with the adsorbent. The dilution, however, results, as noted before, in losses of the volatile solvent, and in difficulties in separating the solvent from the oil after the treatment.

The oil to be treated may be preheated in tube stills.²¹² It is also possible, but not highly practical, to heat and digest a mixture of the oil and clay under a reflux condenser;²⁶³ or the clay, as noted before, can be introduced directly into the still with the oil. Some complication arises in the last method from foaming caused by the water in the clay.

The optimum temperature of treatment varies within a rather broad range and must be determined experimentally for each stock and adsorbent. It usually lies between 250 and 400° F. for low-viscosity stocks, although

in some instances it has been recorded that better results are obtained at lower temperatures.⁸⁹ For heavy residual stocks the temperature may be as high as 600 to 750° F. or even the temperature of the decomposition of the oil. Such high contact temperatures may be used on Pennsylvania residual stocks. If any of the oil is cracked, the low-boiling fractions are removed from the main body of the oil, usually by blowing the hot oil with superheated steam as the oil emerges from the system. The less efficient clays are generally used at lower temperatures than the more efficient clays.

Prutzman in one patent specifies heating the oil with the clay to the temperature of decomposition of the oil,²⁰⁸ and in another patent, heating to above the vaporizing point of the oil.²¹¹ Weir specifies the temperature of the decomposition of any acid sludge that may be left in an oil treated with sulfuric acid.²⁸⁸ Stratford²⁵¹ recommends that the oil and clay be heated separately and then mixed. Delbridge and Dure²⁵ contact at below 212° F.

The time of contact is variable, but it is usually longer for the less efficient clays. It must be determined experimentally for each clay and for the type of agitation. Kalichevsky and Ramsay¹⁴⁰ show curves of the time-temperature relationship of several clays and residual stocks which may be considered typical. In general, the time of contact is less important than the temperature for decolorization of the oil.

In one patent²¹⁰ it is specified that the oil is to stand in contact with the adsorbent until all air is displaced from the pores of the adsorbent before the mixture is heated in order to avoid the oxidizing action of air at high temperatures.

Removal of Adsorbent from Oils. Filters

The clay should be removed from the oil as quickly as decolorization occurs to avoid subsequent discoloration of the oil; for this reason continuous treatment is preferable to batch treatment. In order to shorten the time of treatment in batch processes, the cycles are made short; usually not over 125 barrels of oil are treated at one time. The oil and adsorbent are generally cooled to below 300° F. before they are filtered in order to prevent reversion in the color of the lubricating oil on exposure to air.

The spent clay can be separated from the heavy oil by filtering or possibly by centrifuging. The centrifuging processes are as yet not extensively used.²⁹⁹

The following types of filters are used for separating treated oils from the spent clay: the cell type, such as Sweetland or Kelly pressure filters, the plate and frame filters, the rotary continuous filters, and sand filters. The cake capacity of a filter is, in general, more important than the rate of flow. For pressures not over 50 pounds per square inch, Sweetland

filters should be used; for pressures greater than 50 pounds, Kelly type filters are more suitable. Both types permit washing, steaming, and drying the cake while it is on the filter. For especially high pressures and temperatures, the plate-and-frame type filter is recommended. In the filtering operations, the oil can be kept hot by admitting steam above the oil level in the casing of the filter at pressures up to 200 pounds per square inch, or by using larger units and maintaining a high rate of throughput.

Various filters are described and compared by Zehring.²⁰⁰ Filters suitable for lubricating oils are discussed by Truesdell.²⁰⁷ Methods for calculating filter capacities are given by Wait.²⁰⁰ Filter rates of clay-oil slurries were investigated by Bible, Witte, and Donnell,²⁰ who found evidence that Poiseuille's law does not describe closely enough for engineering calculations the rate of flow through both the filter cloth and filter cake. Canvas filter cloth usually gives very good service for oils which are contacted with the clay in the neutral state, but monel cloth should be used if the oil is contacted with clay directly after acid treatment, because the acid fumes quickly destroy the canvas.

It is frequently preferable to apply a thin coat of special filter aid to the filter before the oil is admitted,⁶ or to add the filter aid to the oil and let it accumulate with the adsorbent material. With the finely divided clays, the filter cloth, or screen, may quickly become plugged, but it can usually be cleaned by releasing the pressure and blowing air countercurrent to the flow of the oil. The most important property of the filter aid is its high porosity, and this property should not be sacrificed for high adsorption or high coagulation properties in choosing a filter aid.³⁴

Some patents recommend the removal of the adsorbents from the oil in two steps: first by filtration, centrifuging, decantation, etc., and then by repeating the same procedure after adding facilitating agents, such as electrolytes (sodium phosphate or carbonate, potassium chloride, etc.) or other adsorbents (fuller's earth, silica gel, etc.);¹²⁷ but such a complicated procedure is usually too expensive for commercial practice. At the last the oil may be again passed through blotter presses in order to remove the last traces of fine clay and possibly moisture which may remain in the oil after the first filtration. It should be noted that although the solubility of water in the hot oil is extremely small, it may be sufficient to form a cloud after the oil is cooled. Blotter filtering is generally effective for removing such moisture.

In operating the filters, only a little pressure is applied at the start, but it is gradually increased. The capacity of the filters varies between 15 and 150 barrels per day, depending on their size and the amount of adsorbent used on the oil.

In the vacuum filtration of light oils, the Wait circulating system has special merit in the prevention of loss of the volatile constituents. In this system the air and vapors drawn through the filter are compressed and returned to the outer shell, which is maintained at about atmospheric pressure.

Sand filters are used mostly for filtering light distillates, such as gaso-

line or kerosene. In the Hardinge type of filter, which has a bed of sand as filter medium, a revolving spiral scraper removes per revolution about 0.01 inch of sand from the surface in addition to the clay which has collected on the sand. The scraper eliminates shutting down the filter except for refilling with new sand.

Removal of Light Oil from Spent Contact Clay

After the agitation period, a finely divided contact clay or earth settles completely from gasoline or kerosene, but still retains some of the oil. The amount of oil retained varies with the type of adsorbent, the period of settling, etc., but it is often about equal in weight to the adsorbent itself. The oil retained by the clay is seldom recovered in practice as the quantity is usually insufficient to warrant the increased expense.

It has been found that by agitating a light oil-clay pulp with from two to five volumes of hot water, about 90 per cent of the oil is displaced from the clay. With proper equipment steam agitation can be used; and if any of the oil is volatile at 212° F., the small amount distilled can be condensed and saved. Moreover, Dunham⁶¹ has shown that if a definite amount of cold water is stirred thoroughly into the oil-clay pulp, the oil is almost completely displaced, the clay being preferentially wetted by the water. It is imperative that only enough water be added to make an extremely stiff water-clay pulp; the addition of more than this amount makes a thin slurry, which emulsifies the gasoline. The amount of water, usually about 75 per cent of the dry weight of the clay, can be determined for any clay-oil pulp by adding gradually a measured amount of water to the pulp while the mixture is stirred thoroughly. Sulfuric acid acts as water in displacing the oil.

Comparison and Relative Costs of Refining Lubricating Oils by Contact and by Percolation Processes

Davis,⁵⁵ in a very informative paper on the principles of the contact filtration of lubricating oils, discusses a comparison of the costs of producing a given change in color in a heavy oil by contact and by percolation methods. His comments and data are given below.

"In order to compare the two methods let us assume that a given cylinder stock neutralizes by contacting to a color of $\frac{1}{2}$ Tag-Robinson, and the problem involved is to decolorize it to a finished color of 1. This can be done first by using sufficiently more clay in the first contact to finish to a 1 color. This will require contacting to $1\frac{1}{4}$ color to allow for darkening during dewaxing and reducing. This additional (Riverside) clay amounts to about 14 per cent. Second, the oil can be finished as $\frac{1}{2}$ color and then recontacted to make 1 color. This would require $14\frac{1}{2}$ per cent of River-

side clay. Third, the $\frac{1}{2}$ color finished oil can be percolated through coarse fuller's earth to give 1 color. Experience shows that this requires about 133 pounds of Riverside clay per barrel when using an average clay (1 to 40 burns if a multiple hearth furnace is used).

"Table 60 represents the comparative cost of such an operation. The direct expenses cover labor, steam, power, normal maintenance, etc., but do not include plant overhead nor investment charges.

"In the first case the extra clay is added at the time of the first contact and, therefore, carries only a nominal operating expense to cover the extra labor, pressure filtering, etc. However, if the oil is decolorized at this point, the 20 per cent petrolatum content must also be treated, thus materially increasing the cost of decolorizing per barrel of finished bright stock.

"These costs indicate that until a method of reclaiming used fine clay or until a relatively cheap, highly efficient, decolorizing material is available, the percolating filtration method will prove more economical for final decolorization."

Table 60. Relative Cost of Decolorizing Bright Stock from $\frac{1}{2}$ to 1 Tag-Robinson Color.

	I Single Contact	II Double Contact	III Percolation
Clay used per barrel (pounds)	44	46	133
Clay cost per ton	\$14	\$14	\$20
Net cost per ton	\$14	\$14	\$ 0.50
Times used	1	1	40
Cost burning			\$ 0.85
Clay cost per barrel of charge	\$ 0.308	\$ 0.322	\$ 0.090
Cost per bbl. direct operation	.050	.196	.270
Total cost per bbl. charge	.358	.518	.360
Yield finished bright stock	80%	98%	98%
Cost of decolorizing 1 bbl. finished bright stock	\$ 0.448	\$ 0.528	\$ 0.367

Funsten's data⁸⁵ concerning cost of percolating oils through clays should be consulted by those interested in this phase of the problem.

Filtrol Fractionation. Distilling Oil from Contact with Activated Clay

The Filtrol Fractionation process is recommended by the Filtrol Corporation particularly for refining lubricating oils. In this system a portion of the lubricating oil stock being pumped to the fractionator is by-passed to a mixing tank where the clay is added. This portion of oil bearing the fine clay is then united with the main stream of oil, and the whole passed through a heat exchanger, then a pipe heater, and finally charged into the fractionating tower at around 675° F. The various cuts are taken from the tower, and the heavy bottoms containing the clay are sent to a surge tank and

then to a vacuum filter, where the spent clay is removed. The clarified bottoms are then sent to storage.

The process is different from the normal contact process in that the stock is first treated, and then the lubricating oils of different boiling points and viscosities are segregated from one another in the fractionating column. Only the heavy residuum needs to be filtered from the clay. The process is often much more economical than the normal process for it requires less refining equipment and less fuel. However, for some types of stock, this advantage may or may not be offset by the lessened flexibility of the process, because the quantity of clay used is necessarily adjusted to the requirement of the major product, and the color of the other fractions is fixed by that requirement.

Claims are made that the process is applicable to a large variety of substances, such as crude oils containing lubricating-oil fractions, solvent-treated stocks, acid-treated long residuums, dewaxed bright stock solutions, and pressed oils. Description of the Filtrol Fractionation plant operated by the Pennzoil Company at Rouseville, Pa., is given by Albright,⁵ and of the Richmond, Calif., plant of the Standard Oil Company of California by Moore and Gwyn.¹⁸² The latter article contains a description of the continuous vacuum rotary drum filter used for separating the clay from the oil. The Monel metal cloth of the filter is precoated with a 3-inch layer of diatomaceous earth. Each revolution of the filter removes about 0.0004 inch of this precoat in order to renew the surface.

The addition of adsorbents to the oil charged to a still was recommended as early as 1868 by Sterry, Lambe, and Fordred;²¹⁰ similar processes, some of them restricted to charcoal, have been patented at various times by Goldwater,¹² Johnston,¹⁰⁰ McGowan,¹⁰¹ Aylsworth and Dyer,¹² Loomis,¹⁰² Baynes and Fearenside,¹⁰ etc. Some of the processes specify distilling the oil from adsorbents acidified with sulfuric acid,¹⁰¹ or mixed with alkalis.⁷⁰ Distillation of cracked gasoline from fuller's earth for removing gum-forming constituents has also been patented.¹⁰⁸

VAPOR-PHASE REFINING WITH ADSORBENTS

Adsorbents have been used for the refining of relatively light petroleum products, especially cracked gasoline, in the vapor phase. The adsorbents are most economically applied to the vapors between the still and the condensers. Because of the high treating temperatures, the action of the adsorbents on the vapors is more energetic than on the condensates at ordinary temperatures. The polymerized products formed in the vapor-phase treatment can easily be removed from the main body of the gasoline by dephlegmation or partial condensation and need not contaminate the finished product.

The primary purpose of vapor-phase refining of cracked gasolines with adsorbents is improvement in color and odor²⁰⁴ and reduction of gum.

The iodine number incidentally is lowered slightly because of the removal and polymerization of some of the unsaturated compounds.⁹⁶ Some of the adsorbents decrease the sulfur content slightly, although actual desulfurization, which is claimed in some patents,⁵⁶ cannot be normally expected. Some desulfurization is claimed from the addition of metallic oxides to fuller's earth which is used at high temperature for the decolorization and degumming of the oil.⁹⁶

Vapor-phase refining of cracked gasoline with adsorbents is simpler than liquid-phase refining. The necessity of re-running the treated distillates is avoided; and when this process is applicable, the total cost is less than in the liquid-phase methods. Different adsorbents have been reported to be suitable for use in vapor-phase refining; these are fuller's earth,²⁹⁰ boneblack,⁹⁵ charcoal,⁹⁵ magnesite,³⁸ iron oxide or Weldon mud,³⁸ bauxite,¹⁰⁹ aluminum oxide,¹²⁰ aluminum hydroxide,¹¹⁰ clays,¹⁰⁹ minette, which is an iron ore containing phosphorus,²³⁵ reduced bauxite, brown iron stone, and other minerals which contain oxides of iron and which are reduced before being used.²²⁵ Combinations of various substances have also been patented, such as silicic acid and lithium chloride,²¹⁸ or fuller's earth and hydrochloric acid.⁶⁰ However, fuller's earth is the only product in extensive use; some of the earths successfully used in the United States are Attapulgus, Floridin, Olmstead (Illinois), and a heavy Texas fuller's earth.

Two major vapor-phase refining processes are now in use; the older is the Gray Process, and the one recently developed is the Houdry Catalytic Treating Process. These processes are described below.

Gray Vapor-Phase Treating Process

Many patents have been issued for apparatus and methods of vapor-phase refining.¹⁶⁵ Although the older vapor-phase process is often inadequate in itself, its efficacy can be increased, if need be, by subsequent treatment in the liquid phase, such as treatment with sulfuric acid and caustic alkali,¹⁶¹ soda ash,¹¹² acid and clay, water washing, etc. Such additional treatment improves the stability of color in the refined oil, which the vapor phase-treated product often lacks.

The discussion below is restricted primarily to the Gray process, although it may be applied within certain limits to other similar methods for treating petroleum oils.

The temperature of the vapor-phase treatment is usually only slightly above the dew point of the oil, or the temperature required to maintain the gasoline completely in the vapor phase. In treating cracked gasoline by the Gray process the temperature is from 350 to 400° F.,²⁶⁶ unless the distillation is conducted under pressure.³³

The consumption of the adsorbent is decreased by conserving the heat

through the use of properly insulated towers. Truesdell reports that with good insulation the consumption may be one ton of fuller's earth for 600 barrels of cracked gasoline from Mid-Continent crude oil, whereas it may be as much as one ton for 275 barrels of the same gasoline in non-insulated towers. For different types of gasolines these figures vary over an extremely wide range. Many refiners show that from 800 to 8000 barrels of cracked gasoline can be refined with one ton of earth, although some refiners require one ton of earth for 100 to 400 barrels of cracked gasoline,¹⁵⁹ the amount depending on the stock from which the gasoline is cracked, the type of cracking, and the degree of refinement sought.¹¹²

Price and Brandt²⁰⁷ summarize the results of operating the Gray process by the Pan-American Refining Corporation and show graphs in which the color and induction period of gasoline are plotted against the time the clay is in use in the tower. Comparative costs of vapor-phase and other treating processes are given by Mandelbaum and Swanson.¹⁷¹

Steininger²⁴⁷ reports that yields of 5000 to 6000 barrels of gasoline of acceptable color stability can be obtained per ton of clay in the vapor-phase treatment of cracked gasoline under the conditions used in his work. Still higher yields are possible when initial color is the only criterion. High pressures and high temperatures and greater time of contact are favorable to color stability. Oxidation stability is materially increased by clay treating, and a definite relation exists between yield from clay and the oxidation characteristics of the treated product. The induction period is improved up to a yield of 4000 or 5000 barrels per ton of clay.

The gasoline losses have been reported to be as low as one per cent of the charging stock, or even less;¹⁵⁹ but because of the polymerization and necessarily complete elimination of the high-boiling polymerized products in a cracked gasoline rich in olefinic hydrocarbons, the apparent loss of gasoline boiling below a specified temperature may be higher, even three per cent when a relatively large amount of clay is used. However, the polymerized products can be added to the stock supplied to the cracking units, where they can be cracked and reconverted into gasoline. The polymerized products are a yellow, red, or brown liquid, much higher in specific gravity, viscosity, and capacity for absorption of iodine than the gasolines. Failure to remove all these polymers greatly impairs the stability of the gasoline. This condition was not fully recognized in the early operations of the Gray process, and this fact led to a number of conflicting statements in the literature regarding the stability of vapor phase-treated products. The polymerized products are now carefully separated to prevent contamination of the treated gasoline.

The losses in the Gray process are considered to be low because the process removes mainly the diolefins and leaves almost all of the olefins.

The diolefins are conducive to gasoline instability, whereas the olefins are usually sufficiently stable for all practical purposes; in all cases their stability can be further increased by a small quantity of inhibitor.

The color of a high percentage of the cracked gasoline refined in the vapor phase with fuller's earth is good at first, but usually it is not so stable as the color of the gasoline when treated with acid and redistilled. However, it has been noted that certain gasolines may yield a color of 25 to 30 Saybolt, which remains unchanged even through exposure to sunlight for four hours.¹¹²

Bogoslovskii⁹⁰ claims that regular treatment of cracked distillates with acid and alkalis and subsequent distillation with the aid of steam are much superior to vapor-phase refining with floridin because of greater chemical stability of the finished product.

The antiknock characteristics of cracked gasoline are obviously not impaired by the vapor-phase clay treatment since the chemical constitution of the gasoline is practically unaltered except for the removal of the most reactive unsaturated hydrocarbons.

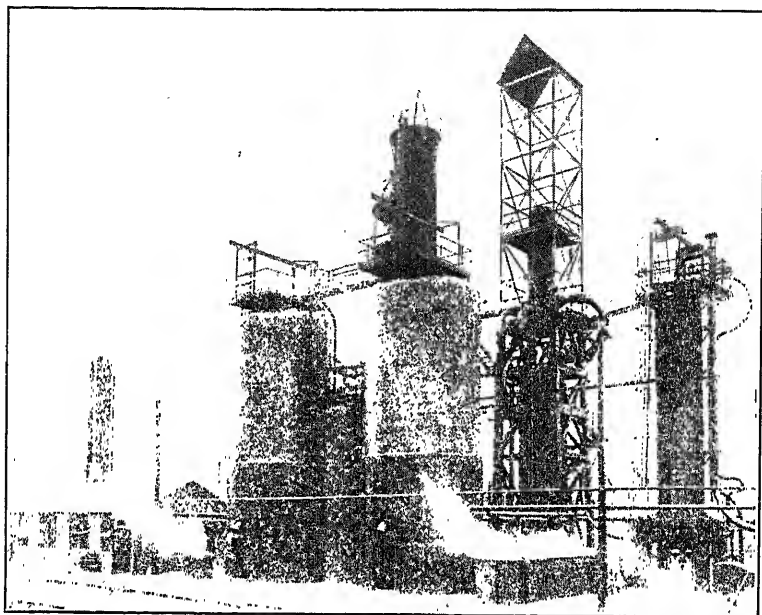
The vapor-phase treatment removes a high percentage of gum and gum-forming constituents, but unless a very large proportion of clay is used, the percentage of sulfur compounds in the gasoline is not materially affected. The Gray process has substantially no effect on the mercaptans in the gasoline.

Table 61. Gum in Cracked Gasoline from Gray Tower.
Gum in Sour and in Sweetened Product after the Indicated Throughput.

“Sour”		“Sweet”	
250 Barrels per Ton Clay			
Glass dish	20 mg.	Glass dish	25 mg.
Copper dish	25 mg.	Copper dish	30 mg.
1000 Barrels per Ton Clay			
Glass dish	20 mg.	Glass dish	20 mg.
Copper dish	25 mg.	Copper dish	25 mg.
2000 Barrels per Ton Clay			
Glass dish	15 mg.	Glass dish	20 mg.
Copper dish	25 mg.	Copper dish	25 mg.
4000 Barrels per Ton Clay			
Glass dish	11 mg.	Glass dish	20 mg.
Copper dish	20 mg.	Copper dish	25 mg.
5000 Barrels per Ton Clay			
Glass dish	9 mg.	Glass dish	11 mg.
Copper dish	16 mg.	Copper dish	17 mg.

Gerstenberger and Goode⁹⁰ submit instructive data on the operation of the Gray process on gasoline from a modified Dubbs unit at the plant of the American Refining Properties, Wichita Falls, Texas. The Gray tower is 10 feet in diameter, 30 feet high, and contains 30 tons of granular

Olmstead clay. Under a vapor pressure of 150 pounds, 750 barrels of 400° F. end point gasoline are treated per day. In one run, after 164,932 barrels of gasoline had passed through the tower, equivalent to over 5000 barrels per ton of earth, the clay still gave the gasoline being treated a color of 30 Saybolt. The gasoline is further treated with alkali solution and doctor solution to remove hydrogen sulfide and to sweeten.



Courtesy, The Gray Process Corp.

FIGURE 18. Two Gray Process Towers in Series Directly Connected with Dubbs Cracking Unit.

Determinations of the gum content of this clay-treated gasoline before and after the sweetening operations were made by means of the glass and the copper dish methods at approximate intervals of 1000 barrels of gasoline per ton of clay. The results of these tests are shown in Table 61. Attention is called to the diminishing gum content in the successive portions filtered. The long run of the one charge of clay is attributed by Gerstenberger and Goode to operating the tower under the higher pressure and the resulting 85 to 100° F. higher temperature than in the usual procedure.

Albright⁴ makes a similar report on the operation of the Gray process in refining cracked gasoline from a Cross cracking unit in the Barnsdall Refinery at Okmulgee, Oklahoma. Of that gasoline about 12,000 barrels

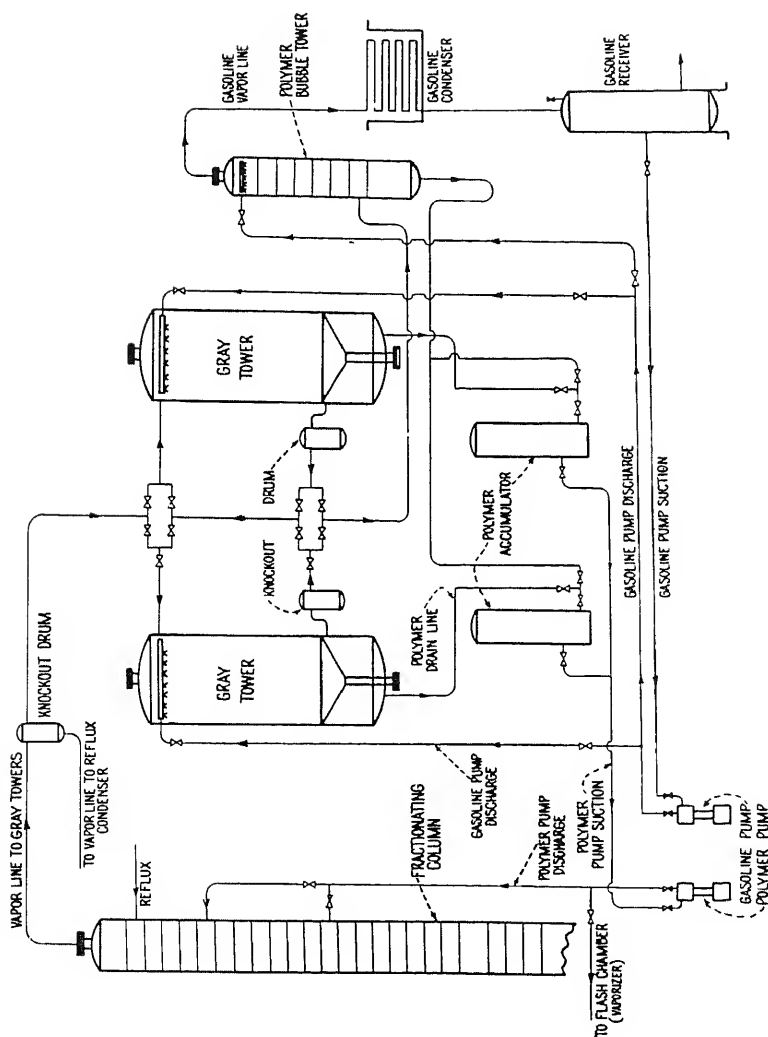


Figure 19. Flow Diagram of Two Gray Towers to Operate in Series or in Parallel Directly with a Cracking Unit.

Courtesy, The Gray Process Corp.

was treated per ton of 60/90 mesh Georgia earth. Other interesting data concerning plant operation have been given by Jones¹³⁵ and Mandelbaum and Swanson.¹⁷⁰

The Gray process in its present state of development gives good results on cracked gasoline from paraffin-base or mixed-base crude oils, but as yet it has not been satisfactory for California cracked gasoline. However, it is probable that with a thorough investigation of the California cracked gasoline, modifications may be found that will make the process applicable to this gasoline.

The first commercial installation of the Gray process was in 1924, and the process is now in extensive use. Its licensed capacity in the United States and abroad is reported as over 70,000,000 barrels a year. Figure 18 shows two Gray towers in series directly connected with a Dubbs cracking unit, and Figure 19 is a flow sheet of two Gray towers so manifolded as to operate in series or in parallel directly with a cracking unit.

Houdry Catalytic Treating Process

The Houdry catalytic treating processes, in contrast to the cracking processes, are designed primarily for refining cracked gasolines. The processes have been under extensive investigation for many years, and already many patents¹²⁴ have been issued that set forth some of their features. The managers of the processes have not yet published broadly the details of the developments; however, many of the important oil companies of the world have studied the operations and are installing commercial units.

Two general types of Houdry catalytic treating operations are described. One gives a sweet product, moderate sulfur reduction, improves the color, the chemical stability, and the lead susceptibility, and reduces the gum. The other gives a substantial sulfur reduction in a high-sulfur gasoline, reduces the "acid heat," and improves the clear and the leaded octane values, the color, and the chemical stability.

In both methods the cracked gasoline is passed in vapor phase at elevated temperature and at pressure up to 50 pounds through a case containing the catalyst. The operation of a case is intermittent with regeneration, and continuous operation is obtained by the use of two or three catalyst cases.

The temperature for the first method of operation is about 600° F., and a special catalyst is used. This process is suitable for the treatment of motor gasoline when a large reduction in the sulfur content is not necessary and for the treatment of aviation gasoline when a large decrease in the acid heat is not necessary.

When a large reduction in the acid heat is required, a different catalyst

is used, and the gasoline is treated at higher temperatures, or at about 800° F. In this second method of operation, some H₂S is given off, so that a caustic wash may also be necessary. The acid heat of cracked aviation gasoline may be reduced to any desired value, and substantial sulfur reduction may be obtained. The treatment may effect an increase in clear octane rating, and it improves the lead susceptibility, the color, and the chemical stability.

Table 62 is illustrative of the results obtained in treating Coastal cracked naphtha by the Houdry second method of operation. The temperature of the treatment was 800° F., and the pressure 50 pounds per square inch. The treated naphthas were fractionated and blended with suitable boiling-point material for motor and aviation gasolines. The data of the last two columns of the table pertain to the finished products. The octane ratings are not shown, but they remain practically unchanged through the treatment, and the lead susceptibility is improved. By varying temperature and pressure, as well as the contact time, the quality of the product may be varied within broad limits.

Table 62. Catalytic Treatment of Cracked Coastal Naphtha by the Houdry Process.

	Untreated Cracked Naphtha	Treated Gasoline	
		Motor	Aviation
Gravity (° A.P.I.)	39.2	48.0	59.4
A.S.T.M. Distillation (°F.)			
Initial	164	95	108
End Point	410	396	301
Sulfur (% by weight)	0.07	0.04	0.03
Aniline Number	66	68	100
Acid Heat (° F.)	81	..	19
Doctor Test	positive	negative	negative
Oxygen Bomb Induction Period (hrs.)	.3	18	11
Copper Dish Gum (mg./100 cc.)	967	3	<1
Glass Dish Gum (mg./100 cc.)	3	1	0
Accelerated Aging Gum (5 hrs., Army Method) (mg./100 cc.)	2
Italian Bromine Index	3.8

The polymerized olefins are recovered and may be used for solvents, for fuel, or for other purposes; practically all the hydrocarbons in the charge can be utilized.

REGENERATION OF ADSORBENTS

Adsorbents used in percolation and in contact filtration differ considerably from one another and require different methods of regeneration. Certain quantities of combined moisture affect the activity of contact clays to a much greater extent than that of percolation clays. The moisture is always removed from the clay at the high temperatures required for regeneration by burning, the only practical method of regenerating the clay.



The moisture in the clays is present as the so-called "free moisture" and "combined moisture." Free moisture is the water adsorbed by the clay without affecting the clay structure. It is given off at temperatures very close to the boiling point of water and is again easily re-adsorbed at lower temperatures.

The combined moisture is released by the clay only at elevated temperatures. Its total removal injures the adsorptive properties of the clay, and the activity cannot be restored by hydration.¹¹¹ Apparently at each temperature a certain amount of moisture is more or less easily given off by the clay and is often referred to as ignition loss.

All air-dried clays contain large quantities of combined moisture. Certain amounts of the combined moisture are expelled when the clay is heated for a certain length of time at successive temperatures. If the moisture content of the clay at the successive temperatures is plotted against the corresponding efficiency of the clay, a very definite curve is obtained which shows the maximum degree of efficiency to which the clay can be reactivated at each burning temperature. Schultze,²³⁶ who has presented important data on the reactivation of clays by burning, shows that the temperature at which combined moisture begins to leave the clay varies widely with the type of clay used. From some clays it can be removed at temperatures below the boiling point of water, but from other clays it is removed only at considerably higher temperatures.

Table 63. Loss of Moisture and Decolorizing Power of Clays on Heating.

Clay A			Clay B		
Temp. (°C.)	Loss of Moisture (%)	Decolorizing Power (%)	Temp. (°C.)	Loss of Moisture (%)	Decolorizing Power (%)
25	0.0	100	25	0.0	100
70	6.7	98	71	14.0	102
102	7.4	90	168	18.5	105
121	7.5	..	204	18.5	87
171	8.0	79	260	19.0	85
288	9.0	80	338	19.0	86
338	9.5	..	432	20.0	76
394	10.5	74	515	21.0	71
538	12.0	63	593	22.0	65
538	12.5	56	621	22.0	63
714	13.0	57	726	24.5	53

Clay C		
Temp. (°C.)	Loss of Moisture (%)	Decolorizing Power (%)
25	0.0	100
65	15.5	110
107	20.0	112
149	21.0	118
260	22.5	107
316	23.0	100
427	23.5	90
593	24.0	83
648	25.0	57

Table 63 summarizes some of the experimental data presented by Schultze.

The tabulation shows that when a contact clay is heated to about 540-565° C. (1000-1050° F.), a suitable temperature for burning the carbon in the revivification process, the decrease in the decolorizing power from the loss of combined moisture would normally be about 25 or 30 per cent. It should be mentioned that the efficiencies of clays in the table are shown on the basis of the weight of the moist clay at each individual temperature. For this reason the efficiency figure would be slightly higher after some of the free moisture is removed because the free moisture has no effect on the decolorizing properties of the clay. This factor may be demonstrated also if the efficiencies are recalculated on a common moisture basis.

The foregoing observations concerning the effect of the moisture on the decolorizing power of the contact clays are also true for clays used for percolation, but to a much less degree. The percolation clays may be heated to relatively high temperatures before the loss in combined moisture is sufficient to have an appreciable effect on their decolorizing power. However, in the usual type of regeneration kilns, local overburning cannot be avoided, and the clay must be discarded after several reburns.

Regeneration of Contact Clays

Adsorbents used in the contact process for refining gasoline or kerosene can be regenerated by heating them to high temperatures with air to burn the carbonaceous material; or they can be regenerated by first extracting the impurities with solvents; or by displacement of the adsorbed oil with substances in which these impurities are insoluble, *e.g.*, with water, and then "burning" the earth. In the first method only a little of the oil retained by the adsorbent can be recovered, but in the other two methods much of it can be recovered. The adsorbents "spent" for certain oils may at times be used for the treatment of other darker and heavier oils, and then after complete utilization they are discarded or revived. In large refineries with a high degree of flexibility, the fresh clay may be used on lighter-colored distillates, and the revived clays only on the darker distillates.¹⁰⁶

Careful laboratory experiments have been made on contact clays, such as those of Death Valley of California, which have been used in decolorizing acidulated (H_2SO_4) gasolines and kerosenes. These clays can be revived 10 or 12 times by washing them with hot water, dewatering, and roasting at 1100 to 1200° F. Their efficiency gradually diminishes, but after these revivifications it is still 60 to 80 per cent of the original efficiency.²⁰⁶ These finely divided clays when heated to 1000 to 1200° F. usually lose much

of the power of decolorizing lubricating oils. The revivification of such clays is described in the patent literature.²⁰⁶

Another method for the regeneration of adsorbents is the extraction of their impurities with solvents. This method is seldom, if ever, used commercially because of the high cost of the solvents and the difficulty of recovering them completely from the clay. When this method is used, however, it offers an almost perfect means of regenerating through many cycles without substantial loss in adsorbent efficiency. Some loss nevertheless occurs because of the extremely slow but gradual accumulation of impurities from the oil; these cannot be completely removed from the clay even with solvents.

Many solvents have been recommended for the regeneration of adsorbents. For effecting complete or almost complete regeneration a combination of two solvents is usually needed. One should be of the polar type, such as alcohol, which is capable of displacing the carbonaceous material from the clay by preferential wetting or adsorption; and the other solvent should be of the non-polar type, such as benzene, which is capable of dissolving the displaced impurities.

The extracting power of a solvent can be measured by its heat of wetting the adsorbent.⁹⁰ The following solvents are named in the order of increasing wetting power: gasoline, benzene, chloroform, and ethyl alcohol.¹⁰⁰ However, it may be noted that this method of differentiating the solvents is not very illuminating as it fails to distinguish substances which have a high solvent power toward the carbonaceous materials from those which have practically no solvent power (ethyl alcohol), but which are capable of removing them by merely displacing them from the adsorbent. Mixtures of gasoline or benzene and acetone¹⁰⁵ or of gasoline and alcohol,^{100, 107} are patented. By using a combination of the two solvents, it is claimed that the adsorbent may be regenerated as many as 30 times without loss in efficiency.⁹⁰ However, the unavoidable loss of solvents during the regeneration procedure is usually greater than the saving gained in regenerating the clay.

Successive treatments with two different solvents rather than with a mixture of the two is also recommended, one with special solvent action for the impurities, and the other for the adsorbed oil.¹⁰⁶ In general, the most efficient solvent for extracting, or rather displacing, the impurities is the one adsorbed most energetically by the adsorbent.

The use of single solvents is much less satisfactory for regenerating clays, as the carbonaceous matter deposited on the clay cannot be completely removed by any one solvent. However, the use of some of them helps to remove most of the oily constituents from the clay and thus facilitates subsequent burning. If the clay is not to be revivified, the single solvent may often be used economically to recover the oil left on the clay. The use of naphtha for this purpose has already been discussed.

The most important of the single type of solvents are the hydrocarbon

solvents. Those of higher boiling points have greater efficiency for regeneration than those of lower boiling points, but obviously they are more difficult to separate from the extracted oil and from the adsorbents.²¹⁴ The use of gasoline and naphtha as solvents is very common.²⁵⁵ As the aromatic hydrocarbons have a high solvent power, benzene, toluene, and coal-tar oils, such as pyridine,²⁴³ have been patented for this use. Among other suitable solvents are carbon bisulfide,²⁴⁸ carbon tetrachloride, and dichloromethylene.¹⁰³ Other patents refer to the use of solvents which displace the oil from the clay by differential adsorption, such as liquid sulfur dioxide,²³¹ alcohols, acetone,¹⁰³ solvents containing an alcohol or ketone group as well as an ether or ester group, such as glycol monomethyl or ethyl ether, etc.

To enhance the solvent power of gasoline, it has been recommended that the clay be extracted at a temperature above the normal boiling point of the gasoline but under sufficient pressure to keep the gasoline liquid.²⁵⁶ When alcohols alone are used, the higher alcohols are preferable on account of their immiscibility with water and better solvent action on the carbonaceous material. Isopropyl alcohol of at least 80 per cent strength is specified by Robinson.²²⁷

The simplest oil displacement agent is hot water.⁶⁸

It may be noted that spent clay, when allowed to age under atmospheric conditions, can be revived to greater efficiency by washing with hydrocarbon solvents than if not aged.

Because of the expensive equipment required for the revivification and because of the somewhat unstable price of new contact clays, refiners have generally preferred to buy new clay, use it once, and discard it. The fact that some contact clays for use in refining lubricating oils lose combined moisture and consequently lose efficiency when heated even to moderate temperatures has further deterred revivification operations. Zublin³⁰⁰ has pointed out many reasons for not reclaiming contact clays. The uses of spent clays are discussed in the literature.¹⁴⁵

Regeneration of Percolation Adsorbents

Adsorbents used for percolation are practically always regenerated by burning. If the clays could not be regenerated, the cost of percolation would be prohibitive. The loss in decolorizing power of the percolation clays on burning is usually much less than that of the contact clays, and the percolation clays can be revived several times before they need be discarded.

After use, the adsorbents are washed with naphtha and steamed, removed from the filters, and charged to the rotary kilns or multiple-hearth type furnaces^{169, 188} where they are roasted at temperatures of 700 to 1400° F. In general, low temperatures are preferable to preserve the

efficiency of the clay. However, the proper burning temperature should always be determined experimentally.

Tellier²⁰⁰ designates a temperature of 700 to 1350° F., but 1020° F. is satisfactory for fuller's earth.¹⁰⁰ Others favor a temperature of 1050 to 1100° F.,²⁰¹ probably a good average.

The heat can be supplied either by passing hot gases through the spent material or, more commonly, by burning the oil retained on the clay and regulating the temperature by a large volume of air or inert gases.²⁰⁴ Excessively high temperatures are to be avoided so as not to sinter the clays and destroy some of their adsorptive power. However, with the conventional type of kiln, local overheating can seldom, if ever, be avoided. Some success has been reported in separating overburned particles of clay from active clay by gravity separators,²³⁸ an operation that is possible because the inert particles have considerably greater density than the active ones.

Attempts have been made to lower the temperature necessary to oxidize and destroy the impurities adsorbed on the clays by adding to the clays small amounts of certain catalysts, but thus far they have not been practical. Lang, Anderson, and Von Fuchs¹⁵⁵ find that the metal catalysts at a given temperature of burning lower the amount of carbonaceous material in the clay; but all of them, with the possible exception of cadmium and aluminum, impair the decolorizing power of the clay. The salts of iron, copper, and zinc are particularly objectionable.

As noted above, only the granular adsorbents used in percolators or in the Gray vapor-phase process are, as a general rule, revived and even the granular earth used in the Gray process is for the most part discarded after it has been used only once.

Bauxite lends itself more satisfactorily to regeneration by burning for it can withstand much higher temperatures than fuller's earth and still retain 80 to 90 per cent of its efficiency.¹²⁵ For this reason refineries using bauxite do not segregate clays after each burning but use the same bauxite over and over again, replacing only the material lost from the mechanical handling. This mechanical loss varies somewhat but is considered to be about two per cent per cycle. However, bauxite is considerably more expensive than fuller's earth, and greater expense is involved for initial replacement of fuller's earth with the bauxite.

Recent developments indicate that the fuller's earths may be revived effectively. Simpson and Payne²³⁹ have described a new kiln for regenerating percolation fuller's earth, designated as the "Thermofor Kiln." They state that it is possible to regenerate fuller's earth 16 times with this unit and still retain about 95 per cent of the original efficiency, as compared

with a reduction of as much as 50 per cent in efficiency after five to ten burns by the conventional methods. When a limited amount of oxygen is used, a "carbonization" of the organic matter adsorbed by the percolation clay occurs, and a carbonaceous deposit is left on the clay, which is described as rendering the clay much more adsorptive than the original unused clay for the coloring matter of lubricating oil stocks.

Regeneration is accomplished by blowing air through a kiln to oxidize partially the carbonaceous material and leave an active carbonaceous deposit on the clay. A close control of temperature is maintained by a controlled flow of molten metal or salt mixture at 850 to 1150° F. through a "bundle" of tubes filling the whole vertical kiln. The solution in the tubes, the heat transfer medium, removes or adds heat to the clay as needed. The spent clay is added at the top of the kiln and moves downward between the tubes of the tube bundle countercurrent to the current of air admitted at the bottom of the kiln. The heat is generated by the combustion of the adsorbed organic matter on the clay.

It is pointed out that two of these units are in operation, one having a capacity of 50 tons of clay per day, and the other 10 tons per day; and a third unit of 120-ton capacity is under construction. The units are much less bulky and are much lighter in weight than the usual burners, and the cost is about 25 per cent less.

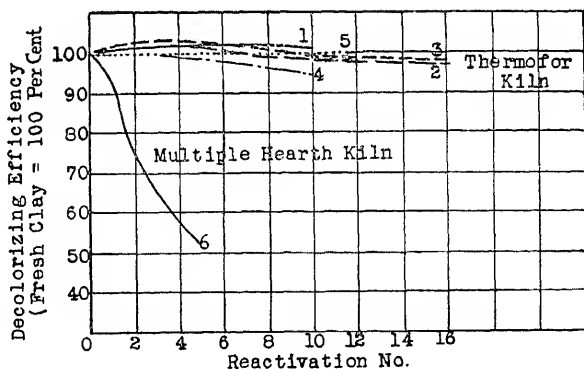


FIGURE 20. Decolorizing Efficiencies of Clays Reactivated by Burning in Commercial Kilns.

- Curve 1—Laboratory percolations with Midcontinent Duo-Sol-treated short residuum.
- Curve 2—Plant percolations with Pennsylvania long and short residua, with and without Chlorex treating.
- Curve 3—Laboratory percolations as a check on Curve 2.
- Curve 4—Laboratory percolations with Midcontinent acid-treated short residuum.
- Curve 5—Laboratory percolations with acid-treated Coastal distillate.
- Curve 6—Conventional operations on a variety of typical Pennsylvania stocks using plant-regenerated clays from a multiple-hearth kiln.

It is also pointed out that "the Thermoform kiln increases percolation-plant capacity by a substantial proportion. For example, in a typical refinery in which clay is regenerated and segregated 10 times and is discarded after the tenth cycle, the average clay efficiency for the entire plant is only 66 per cent based on fresh clay. With a Thermoform kiln in operation and fresh clay being added only to make up for losses (2 per cent per cycle assumed) the clay efficiency of the same plant can be maintained at an average of 95 per cent. This increase in clay efficiency would reduce the washing, loading, and unloading time of the filters by 30 per cent of the normal requirement, and increase proportionately the time for percolation. In this particular case the gain in percolation time represents a 15 per cent increase in the overall filter-plant capacity."

The curves of Figure 20 are presented by Simpson and Payne as illustrative of the improvement of the Thermoform Kiln over the conventional kilns.

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Chapter VII

Refining with Solvents

The refining methods previously described depend more or less on the chemical action of reagents to remove impurities from petroleum oils. In all chemical refining processes, even in refining with adsorbents, the impurities undergo changes in their structure and yield new substances, which are usually of no real value to the refiner. If the impurities can be recovered from the oil unchanged, they can be used in many practical ways; for example, the unsaturated hydrocarbons partly removed in the sulfuric acid treatment could be used as the source material for other chemicals, and the aromatic hydrocarbons removed from kerosene and other light distillates could be used as solvents, paint thinners, etc. Even the extraneous material removed from lubricating oil refining by methods other than solvent refining are of less value as fuel, mainly because of their physical properties, but to some extent because of their chemical properties.

In contrast with the other refining methods described, refining with solvents does not change the chemical and physical properties of the constituents eliminated from the oil. Moreover, the solvent itself is recovered with practically no loss and in an unchanged condition by simple and inexpensive distillation.

The actual refining procedure consists in mixing the petroleum stock with a suitable solvent which preferentially dissolves the undesired constituents, separating the resulting two layers, and recovering the solvent from the raffinate (the purified fraction) and from the extract by distillation.

The simplicity of such a refining method attracted the attention of chemists in the early years of the petroleum industry; but the development was slow because of the lack of cheap solvents, suitable mechanical equipment, engineering skill, and knowledge of the desirable properties of the finished product.

As early as 1863, Tyler patented the refining of kerosene by extracting it with fusel oil.³⁰ Halvorson¹⁶ in 1884 patented the use of amyl and ethyl alcohols for a similar purpose. Loew²⁴ patented the washing of oils with water to remove some of the impurities.

The first successful application of solvents in petroleum refining is credited to Edelcanu, whose patent for liquid sulfur dioxide as solvent for refining kerosene dates back to 1908.¹² It took many years to make this process practical commercially and to demonstrate its superiority over the

conventional processes. The Edeleanu process with certain modifications was later extended to the refining of heavier oil fractions; in this field it now meets the keen competition of other more recently developed processes, although it still is the most practical and widely used process for refining kerosene. At present the total capacity of the Edeleanu plants for refining all types of petroleum oils exceeds that of all other solvent refining plants.

Solvent refining now occupies a very important position in the petroleum industry and is growing rapidly. It is usually combined with other refining processes, as solvents are not always capable of giving the products the best qualities without the aid of other reagents. Thus to some extent the development of solvent refining has complicated rather than simplified the refinery operations. On the other hand, it has contributed to the manufacture of superior products at less expense than possible with the older methods.

Solvent refining operations may be broadly divided into the refining of light petroleum distillates, particularly kerosene, and the refining of the heavier oils, such as lubricating oil fractions. In a few plants, the aromatics which are extracted from certain distillates that are sold as cheaper gasoline or for other purposes are added to premium grade gasolines or naphthas to improve their performance. Such processes are described later under the solvent refining of light distillates. The use of solvents for extracting asphaltic substances and wax from oils will be discussed under the refining of lubricating oils. Descriptions of these processes and their relative position in petroleum refining is presented below. However, one of the authors (Kalichevsky) has published a treatise,¹⁹ "Modern Methods of Refining Lubricating Oils,"* which pertains to the solvent refining of all types of petroleum products, and the reader who is especially interested in the use of solvents for refining oils, dewaxing, de-asphalting, etc., is referred to this work.

Theoretical Principles of Solvent Refining

The solvent refining of petroleum products is based on the differences in the solubilities of the various hydrocarbons and other constituents of the petroleum in certain types of solvents. When a suitable solvent partially soluble in an oil is mixed with the oil, two liquid phases separate out after the concentration of the solvent in the oil exceeds the limit of mutual solubility. One phase is composed of a solution of the solvent in the oil, and the other a solution of the oil in the solvent. As a rule, the solvents used are heavier than the oil; consequently the solution of the oil in the solvent, or the extract phase, constitutes the lower layer, and the solution of solvent in the oil, or the raffinate phase, constitutes the upper layer.

* Reinhold Publishing Corp., 1938.

When the two layers are separated from each other, and the solvent is removed from the oil by distillation, washing with water, etc., the portion of the oil in the solvent solution (extract material) differs in its characteristics from the oil (raffinate) which is recovered from the solution of the solvent in the oil.

In the literature the term "naphthenic layer" is frequently applied to the extract phase, and the term "paraffinic layer" to the raffinate phase. Such nomenclature is somewhat misleading for, as noted below, the naphthenic hydrocarbons tend to concentrate with the paraffinic hydrocarbons in the raffinate layer and not in the extract layer, as would be indicated by this nomenclature.

In general, aromatic hydrocarbons have the highest solubility in the solvents and are, therefore, found in the extract layer. The paraffinic hydrocarbons, on the contrary, are the least soluble and tend to concentrate in the raffinate layer. The naphthenic hydrocarbons are more similar in this respect to the paraffinic than to the aromatic hydrocarbons. Unsaturated hydrocarbons are somewhat more soluble than naphthenes in the solvents. It has been claimed that within certain limits aromatics or olefins, or both simultaneously, can be separated from paraffins and naphthenes, and that naphthenes can be separated from paraffins by the use of such solvents as liquid sulfur dioxide.²⁵ Solubility charts have been prepared¹ which show that extraction of aromatics by liquid sulfur dioxide is limited to mixtures containing less than 50 per cent of aromatics, and that efficient extraction is possible only if the aromatic content is below 25 per cent. However, for all practical purposes it may be assumed that the olefins in general tend to become distributed more or less evenly between the two layers and that they cannot be separated commercially from the aromatics or from the paraffins and naphthenes. The solvents differ slightly from one another in this respect; for example, furfural effects a more nearly complete separation of olefins from paraffins than does liquid sulfur dioxide. Likewise it can hardly be expected that naphthenes can be separated quantitatively from paraffins by using any of the known solvents except at temperatures below the melting point of the paraffins, as described under the solvent dewaxing methods.

In addition to their selective solvent action for certain hydrocarbon compounds, the solvents selectively dissolve the sulfur compounds, nitrogen compounds, and oxygenated compounds. These compounds are recovered from the extract layer. The removal of these compounds is usually desirable for improving the oil, although when the isolation of the aromatics is of primary importance, extraction of the compounds containing sulfur, nitrogen, and oxygen may cause certain inconveniences.

The distribution of the individual hydrocarbons between the raffinate and extract layers is the result of the well-known physical laws of differential

solubilities. For this reason numerous attempts have been made to apply these laws to petroleum solvent refining problems, and very complex mathematical equations have been developed. However, it must be admitted that the results are not successful, and it is doubtful whether they can ever be of more than theoretical interest. This failure is due primarily to the practically unlimited number of individual substances in the oil of varying degrees of solubility. In theoretical equations it is generally assumed that the system consists of two immiscible solvents and the solute. However, the solvents economically available for refining oils are always at least partially soluble in the oil; and, further, the oil dissolved in the solvent changes its solubility characteristics. The resulting system is therefore of such complexity that its mathematical analysis is impossible. Actual extractions with the solvents simulating plant operations must be made to obtain reliable data. A detailed discussion of this subject and an enumeration of various proposed formulas are found in the literature.^{11, 19}

In general, a single, or one-stage, extraction of an oil with the solvent is insufficient to obtain the necessary separation of the various groups of hydrocarbons or undesired constituents because of insufficient differences in their solubilities. For this reason multi-stage, countercurrent extraction systems are used in commercial practice. The number of extraction stages depends primarily on the nature of the solvent and to some extent on other variables, such as the temperature, time, method of contacting, etc. In some instances multi-stage extraction systems are replaced by countercurrent extraction columns, which are convenient and simple to handle.

The major variables involved in solvent extraction are the nature of the solvent and the oil, ratio of solvent to oil, temperature, method of contacting, and time of settling. Solvents differ from one another in their solubility characteristics, and these factors also vary with the temperature. The difference between the solvents may be due to the difference in solvent selectivity or to the solvent power or to both. Proper selection of the solvent is therefore of great importance in securing the most economical operation.

Extraction of Light Petroleum Distillates

Since the most economical method for recovering solvents from oil is that of distillation, the selection of a practical solvent depends to a very great extent on its boiling range. For treating light petroleum distillates two types of solvents are feasible; a solvent that boils at a lower temperature than the lowest-boiling constituents of the distillate, and one that boils at a higher temperature than the highest-boiling constituents of the distillate. At present, only the first type of solvent is used in commercial practice for any of the oils. For the light petroleum distillates, liquid sulfur dioxide is practically the only solvent used; further discussion of

the light oil treatment is therefore limited to this solvent, although in general the discussion is applicable to the other solvents.

As mentioned above, liquid sulfur dioxide was first used as solvent in refining illuminating oils, *i.e.*, kerosenes, and later was used in the refining of other products. It competes successfully with sulfuric acid, however, only on the stocks which require relatively large quantities of the acid.⁷

Brandt⁵ gives approximate cost estimates of treating with solvents; Campbell⁷ shows that the cost varies with the capacity of the unit.

In the earlier practice the chilled, untreated kerosene and the liquid sulfur dioxide were intimately mixed in closed containers by mechanical agitators and then left quiescent for the gravitational settling of the more dense liquid sulfur dioxide and its dissolved material from the less dense aliphatic and naphthenic hydrocarbons. The treatment was usually applied in two or three stages and in a countercurrent manner. In the present development, especially for kerosene or other light oils, the operation is strictly continuous. The volume of the liquid sulfur dioxide used in either method of operation may be nearly equal to or even much greater than the volume of the oil.

Edeleanu and others^{6, 13} have pointed out the advantages of the continuous system over the batch system. A typical operation of a continuous system is illustrated by the accompanying flow sheet (Figure 21).

The distillate to be treated is first dried, degasified by means of vacuum, cooled, and pumped into the gas-tight mixer near the bottom. The cold, anhydrous, liquid sulfur dioxide is pumped into the same mixer near the top. In the mixer the distillate rises, and the heavier liquid sulfur dioxide settles. Intimate contact between the two liquids is provided. The extract, liquid sulfur dioxide with its dissolved material, is continuously withdrawn from the bottom of the mixer, and the raffinate from the top. The two streams of cold liquid from the mixer are first passed through properly arranged heat interchangers to cool fresh incoming distillate and liquid sulfur dioxide and then into multiple evaporators for the distillation and recovery of all the sulfur dioxide. The low boiling point (14° F.) of sulfur dioxide simplifies its recovery.

Sulfur dioxide is usually applied in kerosene treatment at 10 to 15° F. In refining kerosene from asphalt crude oils, the liquid sulfur dioxide dissolves the hydrocarbon compounds having a high ratio of carbon to hydrogen, as exemplified by aromatics and diolefins, and leaves undissolved the compounds richer in hydrogen, such as the aliphatic and naphthenic hydrocarbons. Most of the sulfur compounds are concentrated in the extract layer with the aromatics. Kerosene stock at 10 to

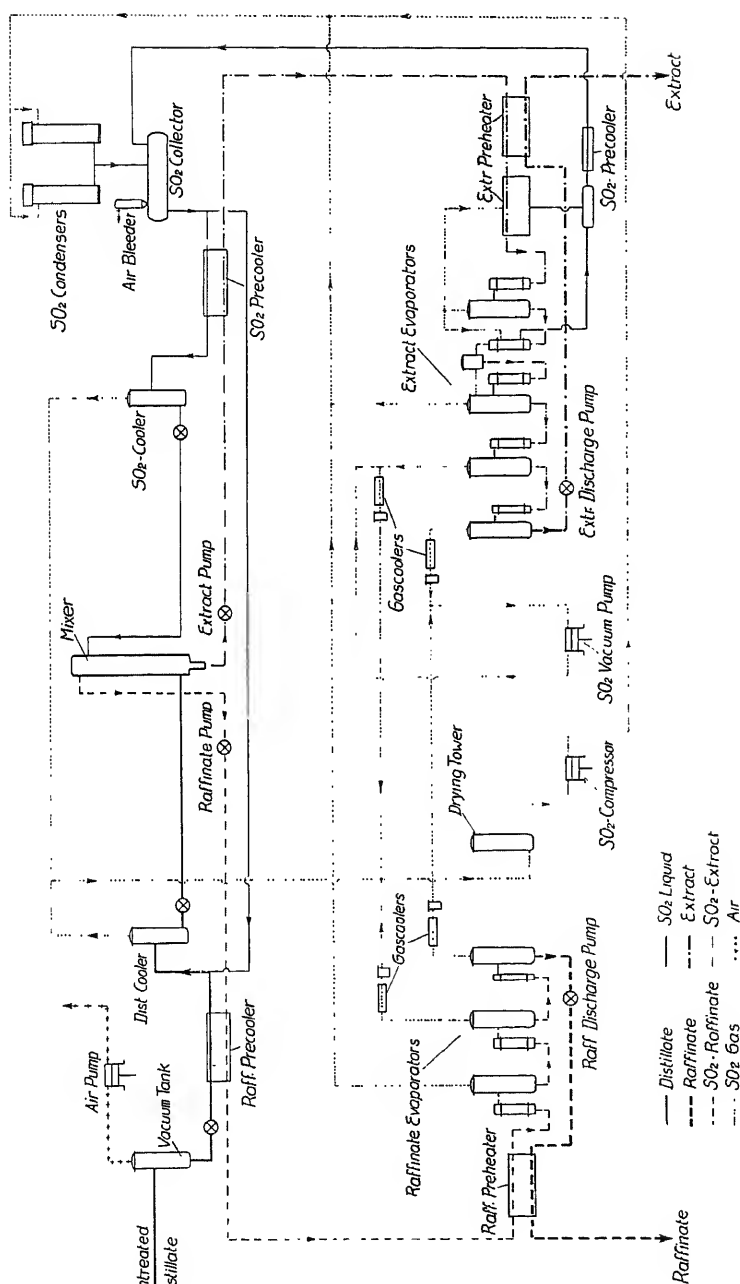


FIGURE 21. Flow Sheet of Edleau Plant for the Continuous Treatment of Light Distillates. Courtesy, Edleau Co., Ltd.

15° F. absorbs from 10 to 12 per cent by volume of the liquid sulfur dioxide; but as more liquid sulfur dioxide is added, two liquid layers are formed. The lower layer is sulfur dioxide and the dissolved hydrocarbons; the upper is primarily hydrocarbons with a relatively low percentage of dissolved sulfur dioxide. The oil from the upper layer has a lower specific gravity (higher A. P. I. gravity) than the original stock, whereas the oil from the lower layer has a much higher specific gravity than the original stock. The quality of the refined kerosene is very similar to that produced by treatment with strong sulfuric acid. The change in gravity of the stock during treatment can be accepted as a fair measure of the improvement made in the burning quality by the treatment. Other corresponding changes in the finished product compared with the original stock are: higher ratio of hydrogen to carbon; higher percentage of saturated compounds; gravity-boiling point curve approaching the curve of a kerosene from a paraffin-base oil; lower sulfur and lower nitrogen contents; less color; less tendency to smoke in burning; less tendency to foul the wicks; etc. The sulfur dioxide treatment may at times be supplemented by treatment with sulfuric acid or adsorbents, such as clays and fuller's earths.

Table 64. Effect of Sulfur Dioxide on Sulfur Reduction in Kerosene Distillates.
(100 per cent by volume SO₂ countercurrent treatment.)

Origin	Sulfur in Distillate	
	Raw Distillate Per Cent	After SO ₂ Extraction Per Cent
West Texas:		
Reagan	0.19	0.07
Winkler	0.45	0.07
Panhandle	0.15	0.05
Pecos	0.625	0.11
Crane Upton	0.49	0.09
Hull	0.10	0.03
Arkansas	0.16	0.025
Venezuela	0.31	0.05
Texas Coastal	0.09	0.03
Oklahoma	0.11	0.04
Trinidad	0.09	0.03
California	0.11	0.04

Liquid sulfur dioxide at low temperatures has a highly selective solvent action for the organic sulfur compounds of petroleum oils. Redwood²⁷ reports the treatment of two samples of Mexican kerosene with sulfur dioxide. One was reduced from 0.6 per cent sulfur to 0.08 per cent, and the other from 0.54 per cent to 0.34 per cent. In a Venezuela kerosene the sulfur content was lowered by 80 per cent. The "aniline point" was also raised by the removal of aromatic compounds. Table 64 gives data obtained in the treatment of 12 kerosene stocks from

different parts of the world but distilled and fractionated so as to have practically the same boiling point range.⁶

These data do not show whether or not a small amount of sulfuric acid was used to supplement the treatment with the sulfur dioxide. Such acid treatment of kerosene is a common practice to remove more of the sulfur and coloring matter.^{14, 32}

Waterman and Perquin³² give experimental results on treating Venezuela, California, and Mexican kerosenes, California transformer oil, Russian oils, and California medicinal oil with liquid sulfur dioxide. Wagner³¹ experimented with a sample of Oklahoma kerosene. Lazar³³ tabulates results on treating various tar and shale-oil distillates, montan wax, and anthracene.

Black and Chappell in one of their patents⁴ specify the use of oleum for treating the oil which is still saturated with the liquid sulfur dioxide, and in another patent³ they state that the amount of sulfur dioxide should be sufficient to dissolve only a portion of the impurities, the remaining impurities being removed by fuming sulfuric acid, which may be added to the oil containing the dissolved sulfur dioxide.

As an example of the effect of the sulfuric acid, a California kerosene stock having 0.35 per cent total sulfur was treated with about 75 per cent by volume of liquid sulfur dioxide, which reduced the sulfur to 0.18 per cent. A treatment with 10 pounds of 66° Bé sulfuric acid per barrel and a wash with weak caustic soda solution further reduced the sulfur to 0.03 per cent. It seems possible that the sulfur removed by the sulfuric acid was not the original organic sulfur of the oil but rather some hydrocarbon and sulfur complex, inasmuch as sulfuric acid in such a small amount does not ordinarily extract so much organic sulfur.

If the kerosene is "sour" to the doctor test after the treatment with sulfur dioxide and acid, it is sweetened by sodium plumbite or otherwise. However, mercaptans, disulfides, and cyclic sulfur compounds are highly soluble in sulfur dioxide and are therefore lowered or removed.³⁴

Less than one per cent of the sulfur dioxide is lost during treatment and recovery,³² and a very commendable feature of the process is the freedom from the conversion of any of the hydrocarbons to sludge.

The Edeleanu process (liquid sulfur dioxide process) is now successfully used in refining Diesel fuel oils. Contrary to the requirements for a good gasoline, these Diesel fuels should contain large percentages of saturated paraffinic hydrocarbons and low percentages of aromatic hydrocarbons in order to decrease the time for ignition in Diesel engines. The ignition quality of a Diesel fuel can be expressed by its "cetane number," obtained by comparing the behavior of the fuel in a test engine with the behavior of a mixture of cetane and alphas-methylnaphthalene. The behavior of the petroleum Diesel fuels in an engine may also be closely determined by their aniline points, for an almost straight line relationship exists between the aniline points and the cetane numbers of the Diesel.² The Diesel index

number is calculated from the aniline point and the A. P. I. gravity of the Diesel, and it is highly indicative of the performance of the fuel in an engine.

Steffen and Sagebarth²⁹ have shown that very good Diesel fuels can be prepared by the liquid sulfur dioxide refining of petroleum oils of suitable boiling point range. Their experimental data are presented in Table 65.

Table 65. Effect of Sulfur Dioxide Extraction on the Ignition Qualities of Diesel Fuels.

	0	Volume Per Cent of Sulfur Dioxide Used	300			
	50	100	150	200	300	
Straight-run Paraffinic Gas Oils:						
Raffinate, % by Wt.	100	92	90	87	85	84
Extract, % by Wt.	0	8	10	13	15	16
Diesel Index Number	68	73	75	77	78	79
Aniline Point, ° F.	185	...	196	202
Raffinate, % by Wt.						
Extract, % by Wt.	100	82	79	76	69	64
Diesel Index Number	0	18	21	24	31	36
Aniline Point, ° F.	58	74	77	80	82	85
	175	...	197	209
Straight-run Nonparaffinic Gas Oils:						
Raffinate, % by Wt.	100	82	77	73	69	55
Extract, % by Wt.	0	18	23	27	31	45
Diesel Index Number	47	58	61	63	65	67
Aniline Point, ° F.	156	...	170	180
Raffinate, % by Wt.						
Extract, % by Wt.	100	79	69	65	61	57
Diesel Index Number	0	21	31	35	39	43
Aniline Point, ° F.	43	57	64	68	70	73
	150	...	185	195
Cracked Gas Oils:						
Raffinate, % by Wt.	100	65	56	54	52	49
Extract, % by Wt.	0	35	44	46	48	51
Diesel Index Number	40	62	73	76	79	81
Aniline Point, ° F.	125	...	173	183
Raffinate, % by Wt.						
Extract, % by Wt.	100	73	61	59	56	48
Diesel Index Number	0	27	39	41	44	52
Aniline Point, ° F.	46	61	72	74	76	78
	124	...	163	172

A large proportion of aromatic hydrocarbons is desirable in gasoline to increase the octane number; as noted above, the Edeleanu process can be used to isolate the aromatics in a relatively high degree of concentration from certain light distillates of suitable boiling range, rich in aromatics, and for which a high octane rating is not needed.

The gasoline hydrocarbons are more soluble in liquid sulfur dioxide than the kerosene hydrocarbons; and to secure efficient isolation of the aromatic hydrocarbons from the lighter distillate, solvent extraction must be carried out at temperatures considerably lower than those used for kerosenes. Temperatures as low as -40 or -60° F. may be necessary in commercial practice. Sagebarth, Broggini, and Steffen²⁸ in a thorough discus-

Table 66. Extraction of a Straight-Run Mid-Continent Naphtha with Sulfur Dioxide.

		Experiment No.			
		I	II	III	IV
Sulfur dioxide used (% by vol.)		40	40	40	40
Extraction temperature (°F.)		0	-20	-40	-60
	Charging Stock	High Octane-Number Stocks			
Yields (% by vol.)	...	12.5	10.6	9.6	9.1
Gravity (°A.P.I.)	53.1	36.7	34.7	33.5	32.2
Octane No. (C.F.R. method)	below 41	82.6	86.2	89.0	91.0
Kauri Gum No.	34.4	71.7	77.3	82.8	88.6
Unsaturates and aromatics (% by vol.)	9.5	70.7	78.6	84.3	89.1
Naphthenes (% by vol.)	15.6	7.3	5.9	4.8	3.4
Paraffins (% by vol.)	74.9	22.0	15.5	10.9	7.5
Sulfur (% by weight)	0.03	0.10
<i>ASTM Distillation (°F.)</i>					
Initial boiling point	225	243	251	251	255
10% point	256	271	276	275	279
50% point	301	309	313	313	314
90% point	359	362	362	361	364
End point	397	412	413	414	414

sion of this subject show that the gasoline extracts may be secured having an octane rating of 80 or 90, or even as high as 100. Tables 66 and 67, giving data on the sulfur dioxide-extracted material from straight-run naphthas of Mid-Continent and South Texas petroleum, respectively, show the effect of the temperature of extraction on the extract material and indicate the feasibility of the process.

Table 67. Extraction of a Straight-Run South Texas Naphtha with Sulfur Dioxide.

		Experiment No.				
		VII	VIII	IX	X	XI
Sulfur dioxide used (% by vol.)		70	70	70	70	70
Extraction temperature (°F.)		0	-20	-40	-60	0 to -60
	Charging Stock	High Octane-Number Stocks				
Yields (% by vol.)	...	46.5	39.5	35.9	34.0	34.0
Gravity (°A.P.I.)	46.8	38.9	36.5	35.0	33.7	33.6
Octane No. (C.F.R. method)	57.9	80.0	84.4	88.2	91.1	90.8
Kauri Gum No.	46.1	68.8	77.2	81.0	82.4	82.4
Unsaturates and aromatics (% by vol.)	31.2	63.1	73.5	80.2	84.0	84.7
Naphthenes (% by vol.)	19.8	13.2	10.1	8.0	6.2	5.8
Paraffins (% by vol.)	49.0	23.7	16.4	11.8	9.8	9.5
Aniline point (°C.)	...	-12.8	-17.7	-19.3	-19.3	-19.5
Sulfur (% by weight)	below 0.01	<0.01	<0.01	<0.01
Freezing point (°F.)	below -60
<i>ASTM Distillation (°F.)</i>						
Initial boiling point	232	239	237	241	247	247
10% point	256	258	259	261	267	267
50% point	292	290	288	289	292	292
90% point	344	338	336	336	337	336
End point	382	398	390	390	394	391

A serious difficulty in using this process to prepare high antiknock gasolines is that it extracts the sulfur compounds together with the aromatics. These sulfur compounds affect the lead susceptibility of gasolines unfavorably and may increase the sulfur content of the gasoline above permissible limits. The process is not applicable to naphtha distillates having a high original sulfur content. Careful investigation should, therefore, precede a decision to install the process in a refinery.

As noted previously, the solvents used in refining the oils are usually separated from the treated oil by distillation, and a certain difference should exist between the initial boiling point of the light petroleum fraction and the boiling point of the solvent. In refining heavy distillates, the solvents obviously must boil below the initial boiling point of the petroleum fraction; the difference should be at least 50-60° F. to permit separation without undue complications. At present, only liquid sulfur dioxide is used for the extraction of such materials as gasolines, although suggestions have been made that very high boiling point solvents be used, such as diacetin (glyceryl diacetate),⁹ etc. The diacetin has not yet been used commercially.

Extraction of Heavy Petroleum Distillates

The use of solvents in refining lubricating oils is a more recent development. However, all the important manufacturers of lubricating oils now use some type of solvent refining.

It may be assumed that lubricating oil stocks contain valuable oil constituents with high viscosity index, low carbon residue, and high oxidation stability, and also objectionable oil constituents, such as asphalt, wax, etc. The latter, which will be referred to in this chapter as the "low viscosity index constituents," must be removed in refining. Obviously the refining operations must vary with the type of oil treated as well as with the specifications for the finished product. However, in a general modern refining process, the lubricating oils must be dewaxed, deasphalted, and extracted with solvents. The subject is further discussed under these separate headings.

Dewaxing of Lubricating Oils

Most of the lubricating oil distillates and residual stocks contain waxes in varying amounts. These must be removed so that the oil will have high fluidity at low operating temperatures. A measure of the proper elimination of the wax from the oil is the "pour point," or the temperature at which the oil ceases to flow.

The pour point may be affected by asphaltic substances as well as by the waxes. The removal of both these constituents is sometimes necessary to secure the proper fluidity. However, the asphalt is always removed in the high-grade oils. The pour point test, which is used for laboratory control purposes, is not necessarily an exact measure of the congealing point of an oil, as the results vary with the size of container, rate of chilling, etc.

The waxes in the lubricating oil stocks may be classified in two types: crystalline, or paraffin, waxes in the petroleum distillates; and the petrolatums, or ceresin waxes, in the residual stocks. The paraffin waxes have a well-defined crystalline structure and usually can be removed by merely chilling the stock and filtering the oil from the wax crystals, but the petrolatums have a microcrystalline structure that makes their separation from the oil much more difficult. Although there is a difference of opinion as to whether the microcrystalline structure should be regarded as an inherent property of the petrolatums or ascribed to the presence of natural inhibitors, nevertheless for all practical purposes the two types of waxes may be considered as differing from each other. The crude oil is usually fractionated at the refinery in such a manner that the distilled lubricating oil fractions contain all the crystalline paraffin wax, and the residuum contains all the petrolatum, or ceresin wax. However, the importance of this fractionation to yield oils containing different types of waxes has disappeared since the introduction of the new dewaxing methods capable of handling both types of waxes, as well as their mixtures.

In dewaxing the distillate stocks, the stock is chilled usually to a temperature equal to or slightly below the pour point desired in the finished oil, and then it is filter-pressed for the removal of the wax. If too viscous, the stock may first be diluted with naphtha so as to reduce the viscosity of the distillate and to increase the filtering rate. If the stock is diluted, the chilling temperature is usually somewhat lower to offset the greater solubility of the wax in the added naphtha. The diluent naphtha is later distilled from the oil.

In dewaxing the residual stocks, the above method is not applicable unless special types of solvents, discussed further below, are used. The wax crystals in these residuums are so fine that they cannot be removed by simple filtration. Two methods have been used for the separation of these fine crystals: one is the cold settling method, now practically obsolete; the second, and newer, is the centrifuging process.

In the cold settling process, the oil is diluted with light naphtha (usually about 70 per cent by volume), chilled, and settled. This process is unfavorably affected by moisture in the oil, by overheating the oil in the distillation process, by faulty acid treatment, and by improper rate of cooling. The viscosity and the specific gravity of the oil solution must be low for the wax particles to settle. Much time is required to secure proper separation; and in order to improve the oil recovery from the separated wax, the wax is again diluted with naphtha and resettled. Even under such conditions much oil is lost, and a large number of settling tanks is required.

In the centrifuging process, the oil is diluted with naphtha, chilled to a predetermined temperature, usually 30-50° F. below the desired pour point

of the finished oil, and centrifuged. Recycling of the wax portion is common practice to recover more of the oil. The quantity of naphtha added to the oil depends on the viscosity of the oil; it is usually about 60-70 per cent by volume in the final mixture. The quantity varies with the chilling temperature, more solvent being needed at lower than at higher temperatures because of the increased viscosity of the oil.

In the foregoing processes, considerable care must be exercised to insure proper crystallization of the wax so that it can be separated from the oil. The rate of chilling the oil to a temperature of about 10° F. above the cloud point of the oil is apparently of no importance, but further chilling to 0° F. should be carefully controlled; in this range the rate of chilling is about 1-2° F. per hour as a minimum, and 3-5° F. per hour as a maximum. It seems that the oil can be chilled below 0° F. at a much faster rate without undesirable effect on the filtering characteristics of the wax. This slow rate of chilling is important for the growth of the wax into large crystals, which can be filtered from the oil.

It should be mentioned that heretofore the centrifuge method was suitable primarily for separation of wax from residual stocks and not for the crystalline waxes of the distilled fractions. The wax of the latter oils forms a hard layer in the centrifuge bowl which is not discharged by the centrifuge. However, special scrapers have been developed recently for removing such waxes from the centrifuges, and the centrifuges may therefore be used for the separation of the crystalline wax from the oil.

The dewaxing methods described above have many unsatisfactory features, such as: the necessity of segregating the paraffin wax from the ceresin wax by distillation before the waxes can be separated; inability to remove the wax from certain types of distillates, such as overhead cylinder stocks; necessity for very low temperatures for dewaxing; and failure to separate the wax sufficiently free from oil with the consequent large loss of oil.

The newer developments in dewaxing include such methods as the use of filter aids, electrical precipitation, and solvents.

The first use of filter aids in dewaxing oils on a commercial scale was in the Weir process.³³ In this process, the oil to be dewaxed is diluted with naphtha, chilled, mixed with filter aid of the type of "Hyflo Super Cel" or "White Speed Flow," and filtered. Up to 15 per cent of filter aid, based on the weight of the oil, has been used. All types of stocks can be dewaxed in this way irrespective of the nature of the wax.

The kinds of material proposed for use as filter aid may be broadly classified as follows: the various infusorial earths, which are added to the oil in the manner described in the Weir process; substances, such as naphthalene, anthracene, etc., which are soluble in the oil at ordinary temperatures but crystallize out of the chilled oil before the wax begins to crystallize;

and chemical reagents, like sulfuric acid, which produce a sludge in the oil consisting of minute nuclei around which the wax tends to crystallize. Sulfuric acid for this purpose has been tried commercially in Europe in the so-called "Russian" method of dewaxing, but with only slight success.

These filter aids have a purely mechanical action in aiding the filtering or centrifuging operations. Recently, however, substances have been proposed which have the property of modifying the crystal structure of the waxes. This type of substance is exemplified by the pour point inhibitors, like Santopour or Paraflo,⁹ which are briefly discussed in Chapter XI. The use of such wax modifiers often simplifies some of the difficult refinery problems.

The electrical precipitation methods have not been tried beyond a semi-commercial scale. In these methods the wax is continually precipitated from the chilled solution by the action of an electric field. As the wax is deposited in the apparatus in a thin layer, it is removed in a continuous manner. The Union Oil Company of California has taken an active part in this development.

In the solvent dewaxing methods, the wax is removed from the solution either by filtering or by centrifuging. In general, all types of stocks may be handled by either of these methods. When the wax is removed by filtration, such solvents are used as benzol-acetone mixtures, or their equivalents, or propane; when the wax is removed by centrifuge methods, the chlorinated solvents of high specific gravity are used and consequently the wax slurry is discharged at the center and not at the periphery of the centrifuge as when naphtha is used as solvent. At present the filtering method is the more popular.

In general, two types of solvents may be employed; namely, the single solvents and the blended solvents. Blended solvents are preferable for increasing the flexibility of the plant operations; they permit the adjustment of the solubility characteristics of the solvent to individual stocks by varying the ratios of the components. Thus a ketone like acetone or methyl ethyl ketone dissolves practically no wax, but does not dissolve enough oil to make it possible to separate the oil from the wax, especially at the low temperatures required in dewaxing. On the other hand, low-boiling aromatic hydrocarbons like benzene and toluene dissolve oils in all proportions but dissolve too much wax to effect separation of the oil and wax. When two such types of solvents are mixed in proper proportions, a blend can be obtained which, under the temperature conditions for dewaxing, has low solvent power for the wax and high solvent power for the oil and can effect suitable separation. A large variety of such solvent combinations can be found, such as ethylene dichloride and chloroform, liquid sulfur dioxide and benzene, furfural and benzene, etc.

In the ketone-benzene process, a mixture containing 25-40 per cent acetone or methyl ethyl ketone, 12-25 per cent toluene, and 40-60 per cent benzene is used. The ratios depend on the characteristics of the oils under treatment. The larger proportion of benzene or toluene necessitates the use of lower chilling temperatures to obtain an oil of a given pour test. The larger volume of solvent gives a lower filtering rate but a better oil recovery. The oil to be dewaxed is diluted with 3-4 volumes of such a mixture of solvents, chilled to about 5° F. below the desired pour point of the oil, and filtered. In this dewaxing process the oil may be chilled at a rate of 30 to 100° F. per hour.

In the propane process of dewaxing, the oil is mixed with propane, chilled to 25-35° F. below the desired pour point of the oil, and filtered. The temperature difference between the pour point of the dewaxed oil and the chilling temperature is thus greater than in the ketone-benzene process, but lower than in the conventional dewaxing methods using naphtha. It is claimed, however, that the so-called self-refrigeration, produced by permitting some of the propane to evaporate from the mixture under vacuum to lower the temperature of the mixture, affords considerable economy in reaching the low temperature for the dewaxing.

The dewaxing processes that employ the heavy chlorinated solvents always use the centrifuge methods for separating the wax from the oil. The best known solvents for this purpose include trichloroethylene and mixtures of ethylene dichloride and benzene. The oil to be dewaxed is blended with the required quantity of solvent and chilled 10-20° F. below the desired pour point of the oil. The chilled mixture is then centrifuged.

The wax separated in the first filtering or centrifuging operation carries some of the lubricating oil, which in part is recovered when additional solvent is added to the wax-oil mixture and the mixture reprocessed, or recycled. This operation is used extensively with the chlorinated solvents.

It should be pointed out that no sharp line of demarcation exists between waxes and lubricating oils. The dividing line between the two is determined by the arbitrarily selected pour point of the oil; thus some of the wax is classified as oil if a high pour point of the oil is accepted, but as wax if

Table 68. Relation Between the Pour Point of the Dewaxed Oil and the Melting Point of the Separated Wax Obtained in Dewaxing a Pennsylvania Lubricating Oil Distillate of 96.3 Saybolt Universal Seconds at 100° F.

Dewaxed Oil		Wax	
Pour Point (°F.)	Yield of Oil (% vol.)	Melting Point (°F.)	Portion of Original Oil (% vol.)
25	87.2	122.5	12.8
20	85.9	120.2	14.1
10	84.1	117.5	15.9
0	82.6	115.8	17.4
-10	81.3	114.3	18.7

a low pour point is required. Similarly the properties of the wax vary with the chosen pour point of the oil, as illustrated in Table 68 from the data of Kalichevsky and Lee.²¹

Table 69, from the publications of Davis and Blackwood,⁹ presents significant data on the influence of dissolved wax on different properties of lubricating oils, especially the effect on the pour point of the oil.

Table 69. Effect of Wax Content on Pour Point Temperature and Viscosity Index of Lubricating Oils.

Oil	A.P.I. Gravity	Viscosity		Pour (°F.)	Visc. Index
		at 100° F.	at 210° F.		
A	29.1	468	62.2	-10	99
A + 4% wax ^a	29.1	450	62.0	20	103
A + 6% wax ^a	29.2	442	62.0	45	105
B	28.9	470	62.2	-10	99
B + 4% wax ^a	28.9	461	62.0	20	100
B + 6% wax ^a	28.9	447	62.0	40	104
C	28.1	498	62.5	-10	93
C + 4% wax ^a	28.0	479	62.4	20	97
C + 6% wax ^a	28.1	471	62.6	40	99
D	28.0	500 ^b	62.9	100	94
D after dewaxing	27.2	522	62.5	20	87
E	27.9	515 ^b	63.5	85	94
E after dewaxing	27.7	532	62.9	10	86
F	28.7	421	62.0	40	110
F + 5% wax ^c	29.3	365	59.0	75	113

^a Samples A, B, C were first dewaxed. The wax removed was then added back for the four per cent and six per cent blends.

^b Viscosity at 100° F. determined from viscosity at 210° F. and 130° F.

^c High melting point paraffin wax added in this case.

The data given in the above publications refer to certain types of oils and do not necessarily apply to all oils.

It may be pointed out that the viscosity of wax at temperatures above its melting point is lower than that of oil of the same boiling range, and the viscosity of the dewaxed oil is, therefore, higher than that of the same oil before dewaxing. The data of Table 70 illustrate the change in viscosity of light Mid-Continent distillates after dewaxing.¹⁰

Table 70. Viscosity Change after Dewaxing.

Pressing Temp. (° F.)	Viscosity (Saybolt Universal Seconds at 100° F.)	
	Before Dewaxing	After Dewaxing
+15	100	114
+ 8	75	82
- 5	66	69
- 5	66	68
- 6	68	74
- 8	70	76
-10	58	63
-18	55	57

Similar changes are observed with stocks of higher viscosity than those shown in Table 70. The increase in viscosity is particularly noticeable in oils containing large quantities of asphalt when they are dewaxed with solvents which remove the wax without simultaneous precipitation of the asphalt.

The viscosity index of the dewaxed oil is generally lower than that of undewaxed oil, but occasionally the reverse apparently may be true. In general, the viscosity index of undewaxed oils should be determined by measuring the viscosities of the oil at temperatures at which the wax is completely molten. With some stocks even the temperature of 130° F. is too low for reliable viscosity determinations because of incomplete solution of the wax. For this reason the viscosity index of an undewaxed oil is frequently of doubtful value.

Freeing Petroleum Waxes from Oil

Finished petroleum waxes should contain practically no oil except for a few of the waxy products, such as vaselines, which are mixtures of oil and wax.

The deoiling methods are different for the two general types of waxes, the paraffin waxes and the petrolatums, and they will be discussed separately.

Oil can be separated from the wax crystals if the temperature of the mixture is gradually increased, and the oil is allowed to drip from the crystals. This is a rather primitive method of separating the oil, but it is used extensively and is known as the "sweating process." More modern methods include separation of oil from the wax by means of solvents, but often they cannot compete economically with the old sweating method.

Before it is deoiled, the wax is usually known as "slack wax." In the sweating process of deoiling the slack wax, the wax is run into the upper part of large pans onto the surface of water, which partly fills the pans. The pans are 20 to 60 feet long and 8 to 10 feet wide; they have a horizontal screen, or grid, near the bottom. After the wax is chilled and solidified, the water is withdrawn from beneath, and the wax collects on the screen in the pan. The wax is gradually heated on the screen, and the oil which separates from the wax is drained from the pans. The temperature of the wax is controlled by cold or hot water passed through coils located above the screens but below the surface of the wax cake. The rate of heating should be approximately 1° F. per hour for most complete removal of the oil.

The oil from the pans is usually collected in two separate fractions: the "foots oil" separates first and contains a relatively small quantity of the wax; the "intermediate cut" separates as the final oil and contains rather

small quantities of oil, large quantities of low melting point waxes, and some of the higher melting point waxes. This intermediate cut is usually recycled to separate the wax from the oil.

In the solvent-pressing process of separating the oil from the wax, the slack wax is dissolved in one-half to $1\frac{1}{2}$ volumes of naphtha, chilled, and passed through filter presses. The solution may be recycled for further separation of the oil and wax or for separation of the wax into several fractions of different melting point. These filter press methods always yield larger quantities of wax than the sweating methods, although generally they are rather expensive and cannot always be justified economically.

The ceresin waxes, or petrolatums from dewaxing the residual stocks, cannot be sweated because they do not form large and well-defined crystals. These waxes are therefore first dissolved in suitable solvents, the solution chilled, and the solid wax separated from the oil by filtering or centrifuging processes. In commercial practice the petrolatum is either dissolved in naphtha, chilled, and centrifuged, or it is dissolved in a solvent like a benzene-acetone mixture, chilled, and filtered.

Deasphalting Petroleum Oils

The asphaltic substances in petroleum oils may be classified arbitrarily according to their solubilities in the different solvents as: carboids, carbenes, asphaltenes, and resins. Of these groups carboids are the least soluble, and resins are the most soluble. Besides these general groups, there are also the asphaltous acids or asphaltous acid anhydrides, which have solubility properties similar to the above and can be titrated with alkali hydroxides. In general, carbenes and carboids are absent from most of the crude petroleum; the following discussion is therefore restricted primarily to asphaltenes and resins. For further discussion of the carbenes and carboids, the reader is referred to Kalichevsky and Fulton.^{19, 20}

The asphaltic substances are removed from stocks in preparing the refined products. In refinery practice the degree of removal of asphaltic substances from lubricating oils is most frequently measured by the decrease in the carbon residue (or coke number) of the oil rather than by the solubility measurements. The two methods do not give concordant results, however, and no exact correlation between them exists.

If asphalt is defined in terms of the carbon residue, two types of asphaltic substances are distinguished, which, in accordance with the nomenclature adopted for the gum content of gasoline, may be defined as "preformed" and "potential" asphalt. The preformed asphalt is that part of the asphalt represented in the carbon residue which is actually present in the oil and merely remains as a residue when the volatile constituents are evaporated. The potential asphalt is that part of the residue which is formed in the oil

by cracking or other process, such as the partial oxidation of the less stable volatile components of the oil. Within certain limits the "preformed" asphalt may be considered a measure of the asphaltenes present, and the "potential" asphalt a measure of the resin content of the oil. Such generalizations should not be considered entirely correct, but they are used to simplify somewhat the very complex subject.

The deasphalting processes pertain primarily to the removal of the preformed asphaltic substances, and the solvent refining methods proper pertain to the removal of the potential asphalt. However, some of the potential asphalt may be removed in deasphalting operations, and some of the preformed asphalt may be removed during the subsequent solvent refining although with much less efficiency. It should be remembered that it is impossible not only to make a sharp distinction between the various asphaltic substances but to draw sharp distinctions between the resins and the oil; for this reason, all the nomenclature thus far developed is highly artificial. In the preparation of a refined lubricating oil of certain specifications, some of the asphaltic substance may be considered as part of the oil and therefore not to be removed; but if the oil must be refined to meet more rigorous specifications, such asphaltic material definitely falls within the classification of asphalt.

Different methods are used in deasphalting an oil, such as distillation, solvent precipitation, and treatment with clay, sulfuric acid, and metallic chlorides.

Special distillation units have been developed in which the oil is rapidly heated in a tubular furnace in contact with different vapor carriers, steam, kerosene, etc., to a temperature sufficiently high to effect a little cracking of the oil. The oil is then flashed into a fractionating column, and the oil removed from the asphalt by the vapor carriers. The amount of actual cracking of the oil is kept at a minimum by decreasing the time of exposure to the high temperatures.

Deasphalting by means of clay, sulfuric acid, and other similar reagents has been described earlier in this book and need not be repeated here.

In the solvent deasphalting method, such solvents as propane are used to precipitate the asphalt from the oil. It is generally believed that the asphaltenes are in colloidal solution in the oil and stabilized by resins, the so-called protective colloids. The use of propane renders the colloidal solution or suspension unstable, and the asphalt consequently separates.

In propane deasphalting, the oil is mixed with a relatively large quantity of propane, sometimes as much as 900 per cent by volume, and the mixture settled at 120-130° F. The choice of the settling temperature depends on the degree of asphalt separation desired, and varies within rather

wide limits. When propane is used for dewaxing rather than for deasphalting, the settling temperature is usually below 70° F.

In order to increase the yield of oil in these operations, the propane is applied in a countercurrent manner, *i.e.*, the precipitated material from a previous settling operation is washed with fresh propane, and the fresh propane solution is then applied to a fresh oil charge. The precipitated asphalt is usually sufficiently fluid to be removed from the settling tank by pumping. After the asphalt is removed from the settling tank, the oil may be chilled, and the wax separated, as described above.

At present propane is the only deasphalting solvent of commercial importance. However, several other solvents have been proposed for this purpose. Of these the aliphatic alcohols appear to be the most promising, although in general they are considerably less efficient than propane. The alcohols require lower deasphalting temperatures than propane, and this feature increases the difficulty of separating the asphalt from the wax if both are present in the oil. The viscosity of the alcoholic solutions is also relatively high, and the separation of asphalt or wax from the oil is thus more difficult. The losses of oil are consequently higher, and larger quantities of alcohols are required to improve the yield of oil and to effect sharpness of separation between the oil and asphalt or wax.

Amyl and butyl alcohols are usually recommended for deasphalting and dewaxing. They may be used alone or in mixtures with other alcohols or solvents. The use of mixtures is frequently advantageous for a better adjustment of their solubility and precipitation characteristics, as described under the dewaxing solvents. Alcohols containing larger alkyl groups than amyl alcohol are seldom used unless they are mixed with lighter alcohols or with other solvents because such alcohols require very low temperatures for precipitating the asphalt, and the viscosity of their solutions is very high. The low-boiling alcohols have insufficient solubility for the oil and are therefore of little value.

Although propane is now considered the only commercial solvent suitable for both the deasphalting and the dewaxing operations, economic considerations often favor other solvents for the dewaxing, even if propane must be used in subsequent deasphalting and solvent refining operations, as in the Duo-Sol process described below.

Liquid propane in many respects may be regarded as exceptionally light naphtha. Its dewaxing and deasphalting properties are in accord with the known properties of the low boiling point naphthas that are liquid at normal pressures and normal temperatures. These considerations had earlier suggested the use of propane as a diluent instead of naphtha in the refining of oils with sulfuric acid or adsorbent clays. Commercial experience shows that very marked advantages are gained from the use of propane rather than

naphtha solutions in treating oils with the above reagents because of the added effect of the propane in deasphalting the oil. However, careful economic calculations are necessary before such processes are accepted in the refinery because of the greater investment necessary for the high-pressure equipment and the cost of the propane.

Solvent Refining of Lubricating Oils

Although solvents are used in many refinery operations, such as dewaxing or deasphalting, the term "solvent refining" is usually restricted to the use of solvents for separating the less desirable oily constituents from the more desirable oily constituents of the oil. In the lubricating oil stocks these undesirable constituents are largely aromatic in nature. These aromatic constituents are believed to contribute to the oil poor viscosity-temperature characteristics (low viscosity index), low oxidation stability, and a tendency to form carbon residues. The removal of the aromatic constituents from an oil results, therefore, in the general improvement in all these properties.

Although the foregoing discussion tends to ascribe all the undesirable characteristics of a lubricating oil to the aromatic constituents, it must be understood that this generalization may not necessarily be entirely correct; the actual chemical nature of the higher-boiling fractions of the oil is not definitely known. The undesirable constituents in the lubricating oils are thus grouped with their aromatic contents primarily to simplify the chemical conceptions of the solvent refining processes.

Table 71, from the work of Kalichevsky, Simpson, and Story,²² illustrates the general upward trend of the qualities of lubricating oils from 1932 to 1937 through solvent refining.

However it is pointed out that when the inherent differences between the solvent refining and the acid treating processes are considered, it is to be expected that the actual advantages and disadvantages of the two methods may vary for different oils and for the desired qualities of the finished oils.

The solvent processes of refining lubricating oils may be classified as those employing single solvents, mixtures of solvents, and two solvents immiscible with each other (double solvents). The first two types of processes refer to solvent refining proper; the third type, or the double solvent processes, combines both solvent refining and deasphalting operations. In the use of the mixtures of solvents the relative ratios of the different components are adjusted so as to produce the maximum selectivity and solvent power for refining a given petroleum stock to the desired specifications. It should be mentioned that many of the processes which are commonly classified as single solvent processes use mixed solvents for the better adaptation of the solvent properties of the mixed solvents. Therefore, no attempt will be made in the following discussion to differentiate between the

Table 71. Typical Motor Oils.

Mid-Continent Motor Oils

	1932 (Acid-refined)		1937 (Solvent-refined)	
	S.A.E. 40	S.A.E. 60	S.A.E. 40	S.A.E. 60
Gravity (°A.P.I.)	25.7	23.7	28.8	28.0
Pour point (°F.)	20	25	0	5
Flash point (°F.)	430	480	460	515
Fire point (°F.)	490	535	520	585
Viscosity (Saybolt Universal) at 100° F. (sec.)	770	1,765	660	1,437
Viscosity (Saybolt Universal) at 210° F. (sec.)	73	110	73	110
Viscosity index	83	80	100	98
Carbon residue (%)	0.9	1.4	0.2	0.3
Color (Lovibond)	170	240	60	80
Slight oxidation number	17	4	0	0

Pennsylvania Motor Oils

	1932 (Percolated and Dewaxed)		1937 (Solvent-refined, Percolated, and Dewaxed)	
	S.A.E. 20	S.A.E. 60	S.A.E. 20	S.A.E. 60
Gravity (°A.P.I.)	28.4	26.2	31.1	28.5
Pour point (°F.)	5	20	0	0
Flash point (°F.)	430	510	430	540
Fire point (°F.)	485	575	480	610
Viscosity (Saybolt Universal) at 100° F. (sec.)	373	1,736	294	1,543
Viscosity (Saybolt Universal) at 210° F. (sec.)	57	123	55	122
Viscosity index	100	98	117	105
Carbon residue (%)	0.6	1.5	0.3	0.4
Color (Lovibond)	120	300	70	30
Slight oxidation number	4.0	1.0	0	0

single and the mixed type of solvents. It may be added that many of the so-called single solvents are not chemically pure but are commercial products and often contain varying proportions of analogous material. The double solvent process will be discussed separately, however, because it combines both the deasphalting and solvent refining operations.

Many solvents have been proposed for the refining of lubricating oils, but only a relatively few have received commercial recognition because of the many requirements that a satisfactory solvent must meet. These requirements, besides the necessary solubility characteristics, include ease of separation of the solvent from the oil, chemical stability, non-corrosiveness, low freezing point, and relatively low boiling point. The single and the mixed solvents now in commercial use include liquid sulfur dioxide (with or without benzene), Chlorex, furfural, phenol, and nitrobenzene. The double solvent processes are represented by the Duo-Sol process, in which propane is used as the solvent for the oil and cresylic acid as the solvent for the impurities.

Because of its success in the refining of kerosene and light petroleum

distillates, liquid sulfur dioxide was the first solvent used commercially in refining lubricating oils. However, although liquid sulfur dioxide is highly selective, it has insufficient solvent power in commercial quantities to remove all the undesirable constituents from the lubricating oil fractions. This defect has been lessened by adding to the sulfur dioxide aromatic solvents or aromatic constituents obtained from the lighter petroleum fractions originally suggested by Olsen.²⁶ The Edeleanu Company uses mixtures of liquid sulfur dioxide and benzene in refining lubricating oils when high solvent power is needed. Kain¹⁸ has shown that for the refining of certain lubricating oil stocks the use of a limited amount of benzene in the liquid sulfur dioxide improves the selective extraction of the undesirable constituents of the stock and makes a better lubricating oil. From 15 to about 50 per cent of benzene is specified in the sulfur dioxide-benzene mixture. The beneficial effects of the benzene in the sulfur dioxide can be seen in the few data here tabulated from one of Kain's more comprehensive tables.

Table 72. Treatment of Lubricating Oils with "SO₂-Benzene" vs. Straight SO₂.

	Gulf Coast Lubricating Oil Distillate				California Lubricating Oil Distillate		
	Untreated	200 Vol. % Counter- current Straight SO ₂	200 Vol. % Counter- current Solvent Con- sisting of 85% SO ₂ and 15% Benzene	200 Vol. % Counter- current Solvent Con- sisting of 75% SO ₂ and 25% Benzene	Untreated	200 Vol. % Counter- current Straight SO ₂	200 Vol. % Counter- current Solvent Con- sisting of 75% SO ₂ and 25% Benzene
Temp. of treatment (°F.)	...	25	25	25	...	25	25
Gravity (°A.P.I.)	20.8	23.7	24.8	25.3	15.3	21.2	23.3
Viscosity at 100° F.	915	673	615	570	2733	1247	967
Viscosity at 210° F.	66	63	61.5	60.5	86	74	70
Viscosity index	23	53	58	63	below 0	16	37
Conradson carbon (%)	0.24	0.11	0.08	0.06	0.5	0.16	0.07
Raffinate yield (by vol- ume) (%)	...	84	78	74	...	64	48

The benzene-sulfur dioxide mixture aids in the purification of the lubricating oil and extracts more of the hydrocarbons than does sulfur dioxide alone. The benzene and sulfur dioxide are recovered for re-use. This recovery is possible because of the difference in boiling points—sulfur dioxide boils at 14° F., benzene at 176° F., and the lubricating oil at above 600° F.—but the separation of the mixed solvents from the oil is obviously not so easily accomplished as that of the sulfur dioxide alone.

For refining light lubricating oil fractions, such as transformer oils, the addition of benzene to liquid sulfur dioxide is superfluous. These oils can be refined with liquid sulfur dioxide alone, provided the extraction tempera-

ture is sufficiently high; it must be higher than that used in refining kerosenes or in extracting aromatics from the gasolines and naphthas.

For refining lubricating oils for automotive and aircraft engines, the use of the mixed liquid sulfur dioxide-benzene solvent is not extensive.

The four leading solvent refining processes are: the Furfural process, the Phenol process, the Chlorex process, and the Duo-Sol process, described under the double solvent processes. These processes account for more than 90 per cent of the present solvent refining capacity for the heavy lubricating oils.¹⁹ The general features of these processes are given below.

Furfural Process

The Furfural process is used primarily in refining Mid-Continent stocks, although it can be used on Coastal stocks at somewhat lower extraction temperatures and on Pennsylvania stocks at higher temperatures. The treating temperatures usually vary between 100 and 250° F., but for Mid-Continent oils they are about 200° F. Because of the high extraction temperatures, it is usually possible to treat oils without removing the wax and to use countercurrent treating towers instead of multi-stage countercurrent batch equipment. A temperature gradient of 20-50° F. is usually maintained between the top and the bottom of the treating towers to permit efficient counterflow of the oil and furfural without the necessity of constructing especially tall towers. The boiling point of furfural is 323° F., which is sufficiently low to permit expelling the furfural from the oil without heating the mixture hot enough to cause decomposition or polymerization of the furfural.

Phenol Process

In the Phenol process of refining, the phenol is used in the anhydrous condition or with only a little water. At present the general tendency is toward the use of anhydrous phenol, the process of the Standard Oil Company of New Jersey. In this process the oil is contacted with the solvent at 110-200° F., the temperature being adjusted to the special characteristics of the stock. Some few stocks, however, may require temperatures as high as 250° F. As with furfural, these high extraction temperatures make it possible to refine waxy stocks without precipitation of the wax and to use countercurrent treating towers. The reflux is often increased in the treating towers by injecting water at the level of the feed. The water as well as the temperature gradient increases the efficiency of the extraction through a favorable change in the solubility characteristics of the solvent as it progressively extracts the impurities from the oil.

To restore the solvent, the phenolic solution is first distilled; the vapor is that of a constant boiling solution of phenol and water, 91 per cent phenol

and 9 per cent water. The vapor is passed in a countercurrent direction into some of the untreated liquid oil at sufficient temperature so that the water vapor will not condense, although the phenol is absorbed in the oil in a practically anhydrous condition. The boiling point of phenol is 361°F. , which is higher than that of furfural but still sufficiently low to permit separation of the phenol from the light lubricating oil fractions by distillation. The melting point of pure phenol is 105.6°F. , but this relatively high melting point is not particularly troublesome because even small quantities of the extract impurities, such as aromatic oil fractions, lower it very considerably.

Chlorex Process

The Chlorex process is well suited to the refining of the Pennsylvania type of lubricating oils because the solvent power of Chlorex is high even at moderate temperatures. However, as with all other solvents, Chlorex may be used in the refining of Mid-Continent or Coastal stocks by properly adjusting the extraction temperatures. The low extraction temperatures of the Chlorex process usually necessitate dewaxing the oil stocks before they can be treated. Temperatures of 30 to 80°F. are used for treating Mid-Continent stocks, and temperatures of 100 to 120°F. for such stocks as Pennsylvania residual oils. Chlorex (dichloroethyl ether, $\text{CH}_2\text{Cl}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2\text{Cl}$) boils at 352°F. and is easily recovered from the oil by distillation. It does not dissolve over about three per cent of water at room temperatures, and in refinery practice this small amount is not removed from the solvent.

Nitrobenzene Process

The Nitrobenzene process uses as solvent nitrobenzene, which boils at 411.5°F. , or somewhat higher than the solvents mentioned above. Its solvent power is high, and low treating temperatures are required. Even slight refrigeration is frequently used.

Double Solvent Process

The so-called double solvent processes employ two solvents of relatively low mutual solubilities, one of which has a high preferential solubility for the undesirable constituents of the oil, and the other a high preferential solubility for the desirable constituents of the oil, or for the oil proper. The selection of a "paraffinic" solvent for the raffinate phase is somewhat difficult, as not many solvents exist which, when mixed with oil, are capable of forming and maintaining two phases within the desired temperature ranges after such solutions are brought into contact with the second, or so-called "naphthenic," solvent. Although paraffinic solvents are gener-

ally considered to have preferential solvent action for the desirable oil constituents, this assumption is open to question, particularly for lubricating oil stocks that do not contain asphalt. However, in asphalt-bearing stocks the paraffinic solvent helps the precipitation of the asphaltic substances, and the naphthenic solvent extracts the undesirable constituents. With this type of oil the double solvent processes combine the deasphalting and solvent refining operations into one step.

Several combinations of paraffinic and naphthenic solvents have been proposed, but the Duo-Sol process is the only one in commercial use, and it is growing in importance both in this country and abroad. The Duo-Sol process uses propane as paraffinic solvent and "cresylic acid" as naphthenic solvent. This cresylic acid actually has a phenol content of 20-40 per cent. The phenol permits the use of slightly higher extraction temperatures than if the pure cresylic acid were used. The treating temperature is usually between 60 and 90° F., or occasionally slightly higher. The higher temperature often facilitates the settling. The solubility of wax in the propane component is ordinarily sufficiently high to permit the application of the process to the wax-bearing residual stocks of Mid-Continent nature, for which stocks the process is primarily intended, although applicable to other stocks.

Disposal of Solvent Extract Material

Because of the extent of the solvent extraction processes, the problem of disposing of the material extracted from the oil by the solvents has become of great commercial importance. The extract materials from light petroleum distillates, such as kerosene, and those from lubricating oils and from residual stocks are very different from one another, and the manner of disposing of them is peculiar to each. These three types of extracts are, therefore, considered separately.

The extract material from the liquid sulfur dioxide treatment of a naphthenic kerosene has much commercial value; it contains up to 35 per cent or more of aromatics. The boiling point range of the extract material is identical with that of the kerosene stock from which it is extracted, usually about 300-575° F. About 25 per cent of this material has a low enough boiling point range for use in increasing the solvent action of mineral spirits in the manufacture of asphalt paints and in producing uniform quality in these paints. The portion of the extract boiling below 392° F. has some use as a turpentine substitute, and the higher-boiling fractions are satisfactory fuels. As a special example of its use, the extract of a California kerosene, which amounts to about 15 per cent of the kerosene stock treated, is distilled; the fraction boiling up to 400° F. is separated and added to gasoline stock to increase its octane number.

The gasoline produced is usually very satisfactory, although the kerosene extract may have a comparatively high sulfur content. By cracking the higher-boiling kerosene extract material, aromatic hydrocarbons are obtained of excellent quality for use as motor fuels and solvents.⁸ However, cracking of such extracts is always accompanied by high carbon formation because of the aromatic nature of the stocks. A patent¹⁰ specifies the use of the non-resinifiable extract material as an insulating oil for high-tension switches, transformers, etc. Another patent³⁵ has been issued for conversion of the kerosene extract material into oxygenated compounds by oxidation with air. The manufacture of lubricating oils from the kerosene extract by condensing it catalytically with olefins has been patented; the chlorides of iron and zinc are the catalysts.¹⁷

The extract material from lubricating oil stocks previously deasphalted is now used principally for fuel, although possibly in time more useful application may be found. Attempts have been made to convert this material into commercial products by condensation with aluminum chloride, hydrogenation, cracking, etc., but very little progress has been recorded.

The extract from the double solvent refining, the Duo-Sol process, is a mixture of aromatic and asphaltic substances. Because of the complex nature of this material very little effort has been directed to its conversion into more valuable products. It is used primarily as fuel.

The asphaltic material separated from the lubricating stocks in the solvent deasphalting processes is either burned as fuel or occasionally converted into different grades of asphalt.¹⁹

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Chapter VIII

Detonation and Antidetonants

Detonation, more commonly termed fuel knock, is a rather elusive property of fuels which develops particularly at high cylinder pressures. In mild form it is observed as a rattling noise; if more severe, it may result in mechanical damage, overheating of the engine, and other difficulties. In passenger car engines, the noise generally becomes intolerable before material damage results. In aircraft engines, however, where the noise is masked by the unmuffled exhaust, and perhaps also in trucks, overheating, loss of power, and mechanical damage are more serious.²⁴ The knock is familiar to most operators of automobiles. The term is not particularly descriptive of the noise as usually heard in its milder form; the sound is more like the clinking produced by the rattling together of small bolts or pieces of metal.

A thoroughly satisfactory theory of this gasoline detonation has not as yet been advanced, although Professor Dixon of Manchester, England, observed in about 1919 that in the detonation of gases the velocity of the explosive wave was as great as 10,000 feet per second when confined under certain conditions in tubes, whereas the velocity of the flame in gases burning normally would be only a few feet per second. In the first condition all the energy of the gas is instantly released with an explosive effect like that of trinitrotoluene (T. N. T.) with power to shatter rather than with a slowly released power to maintain continued pressure on the cylinder head of the motor. In about the same way the English engineer Ricardo explains the detonation in the motor when he assumes that the burning of part of the gas-charge compresses the remainder of the charge until it ignites spontaneously throughout the cylinder and burns instantly. The combustion of the gases starts slowly at the point of ignition and increases in velocity and temperature with a high pressure frontal wave so that the unconsumed gas beyond the wave is compressed and automatically heated and ignited. This auto-ignition condition produces the explosion wave, which strikes the walls of the cylinder with hammer-like blows, called knock or detonation. When knocking occurs, the temperature rises in the cylinder, and the resulting hotter engine aggravates the detonation conditions. Because of the high temperature, the knocking phenomenon dissipates energy, which

is lost to the cooling water surrounding the cylinder ; hence a loss of power is incurred.

Midgley and Boyd ³¹ explained the mechanism of knocking as being a result of the impact of a high velocity, high pressure gas-wave against the walls and head of the motor cylinder.

Although it is now accepted that detonation is a function of the self-ignition of the gasoline, it is believed that this function is only one of the factors ; an additional important factor is the chemical change taking place in the fuel immediately preceding the combustion, in which there is an increase in active oxygen compounds, such as organic peroxides. The effect of these and other factors is discussed in the literature.⁷⁷

Dickinson of the United States Bureau of Standards very early predicted the present growth and development of high octane fuels in the statement :

“The work of Midgley and his associates in Dayton, leading to the later work of the Ethyl Gasoline Corporation, has been the most important element in promoting general interest in the properties of motor fuels. The original concept of this work was much broader than that of production of a special antiknock fuel and was based on the possibility of increased power and decreased fuel demand if motor car engines could be made to operate at much higher compression rates. A given engine will deliver more power and, incidentally, use less fuel if the compression ratio is raised. The designer, therefore, raises the compression ratio until the engine begins to knock whenever the temperature or the carbon deposits increase. The user then demands an antiknock fuel. Having stopped the knock in this way, the designer may again raise the compression and repeat the process so long as suitable fuels can be found. The problem of antiknock fuels, therefore, is likely to increase in importance.”

Lovell and Campbell and others ⁵⁰ have discussed the greater amount of power and efficiency obtainable by increasing the compression ratio in motors up to a point at which detonation sets in. This detonation establishes the upper limit of power output. Lovell and Campbell developed the data for the curve in Figure 22 by using a single-cylinder engine at constant speed and varied compression ratio on different fuels ranging in octane numbers from 50 to 100. The octane numbers of the fuels are plotted against the maximum power output at the compressions at which detonation began to be noticeable. The unity of measurement is the power output from a fuel of 50 octane number ; a fuel of 100 octane number gave 35 per cent more power under the same conditions, except that the compression ratio had to be increased to develop the power from this better fuel. It can be added, moreover, that the octane number of 100 does not

represent the upper limit of power output, since fuels can be produced with the aid of tetraethyl lead that have octane numbers above 100. The compression ratios used by Lovell and Campbell in developing this curve varied from about 3.5 : 1 to 7.5 : 1.

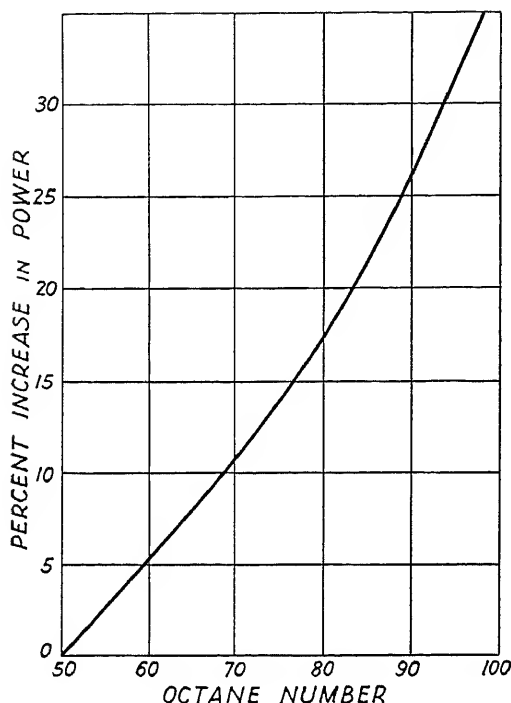


FIGURE 22.

Octane Number Requirements and Power Output.

Recently Klein ⁴⁸ has shown that 100 octane gasoline yields 12 to 30 per cent more power than 87 octane gasoline, and DuBois and Cronstedt ²⁶ have shown that 100 octane gasoline yields 17 per cent more power than 87 octane gasoline. DuBois and Cronstedt find that isoöctane with 3 cc. tetraethyl lead per gallon yields 17 per cent more power than isoöctane alone.

The greater power of the high octane gasoline has thus far been of most importance to the airplane industry inasmuch as the high octane fuels permit long flights with less gasoline and permit transporting a correspondingly greater pay load. The economy of using high octane fuel has been described in the literature.^{28, 38, 39}

The increase in the octane numbers of aviation gasoline used by commercial airlines and the U. S. Army Air Corps are reported by Hubner and Egloff ³⁹ in Table 73.

Table 73. Increase in Octane Numbers of Aviation Gasoline Used by U. S. Army Air Corps and Commercial Airlines.

Year	U. S. Army Air Corps ^a	Commercial Airlines ^b
1938	98*	89*
1937	95	87*
1936	93	85*
1935	91	83*
1934	90	80
1933	87	79
1932	82	73

* Estimated.

^a Army Method.^b A.S.T.M.-C.F.R. Motor Method.

Knocking Characteristics and Lead Susceptibilities of Hydrocarbons

Because of the greater power that can be derived from non-detonating fuels, the views on the most desirable composition and characteristics of fuels have undergone radical changes. In the early automotive period the saturated paraffin hydrocarbons were considered the most desirable constituents; now because of their pronounced detonation in the high compression gasoline motors, they are known, as a class, to be inferior to other hydrocarbon fuels.

The knock characteristics of a fuel in a gasoline engine may be expressed in terms of a standard reference fuel, such as the commonly used mixture of normal heptane (C_7H_{16}) and isoöctane (2,2,4-trimethylpentane). Heptane detonates even at low compression ratios; the isoöctane does not detonate except at high compression. Some definite mixture of the two can be found which exactly duplicates the detonation of the fuel under the specific conditions of the test, and the percentage of the isoöctane in this heptane-isoöctane mixture is taken as the octane number of the fuel.

The ignition quality of Diesel fuels is expressed in terms of "cetene" or "cetane" numbers, which numbers have been developed on a basis very similar to that adopted for measuring the ignition quality of gasoline in terms of octane numbers. However, the cetene or cetane numbers have a significance opposite to that of the octane numbers; because of differences in engine construction high octane number fuels are the poorest, and low octane number fuels are the best for use in Diesel engines.

The cetene number refers to a mixture of cetene (1-hexadecene) and α -methyl-naphthalene (the use of mesitylene, originally proposed in place of α -methyl-naphthalene, has been generally abandoned for economic reasons); the cetane number refers to a similar mixture of cetane (*n*-hexadecane) and α -methyl-naphthalene. The cetene or cetane numbers indicate volumetric percentages of cetene or cetane in the blend. Cetane is normally used because cetene is difficult to purify and is somewhat unstable in storage. The relationship between cetane and cetene numbers has been established as follows:^{1a}

$$\text{cetane number} = 0.875 \times \text{cetene number}$$

The following tabulation gives cetene and cetane numbers for several pure hydrocarbons:^{45a}

	Cetane Number	Cetene Number
Cetene	87.5	100
Cetane	100	...
α -Methylnaphthalene	0	0
Tetraisobutylene	4.5	5
Isooctane (2,2,4-trimethylpentane)	...	17
<i>n</i> -Heptane	57	...

A useful relationship between the aniline point and gravity has been established for evaluating ignition qualities of Diesel fuels on the basis of simple laboratory tests. The relationship is known as the Diesel Index Number.^{7a}

$$\text{Diesel Index No} = \frac{\text{Aniline Point (}^{\circ}\text{F.)} \times \text{Gravity (}^{\circ}\text{A. P. I.)}}{100}$$

An approximate relationship between the cetene number and chemical composition has also been developed for straight-run gas oils:^{10a}

$$\text{Cetene No.} = -0.2A + 0.1N + 0.85P$$

wherein *A*, *N*, and *P* represent percentages of aromatic rings, naphthenic rings, and paraffinic side-chains in the hydrocarbon molecules of the Diesel fuel.

Desirable characteristics of Diesel fuels have been discussed by Blackwood and Cloud,^{9a} who developed a number of interesting curves for fuels, showing relationships between viscosity, mid-boiling point, gravity, hydrogen content, heating value, and cetane number. The curves permit a close estimation of any of the above properties if only two of them are known.

The ignition qualities of Diesel fuels may be improved by suitable addition agents (dopes), which have been reviewed by Broeze and Hinze.^{10a} For the reasons already mentioned, the effect of these addition agents on the fuel is opposite to that of tetraethyl lead, *i.e.*, they promote rather than suppress detonation. Various organic nitrates and peroxides are among the compounds recommended as additives for Diesel fuels; but to the writers' knowledge none of them is widely used. This lack of use is explained partially by the toxic and explosive nature of the agents and partially by the usual ease of preparing Diesel fuels of satisfactory ignition qualities from the refinery stocks. However, with further development of the Diesel engine, specifications for Diesel fuels may become as stringent as those now imposed on high-quality gasolines.

The detonation characteristics of many individual hydrocarbons in the gasoline boiling point range, as well as the lead susceptibility of some of them, have been measured. The data of Tables 74, 75, and 76 were developed by the Research Division of General Motors, Incorporated.^{51, 52}

The term "critical compression ratio" signifies the compression ratio at which an incipient knock¹⁶ is just audible in a single-cylinder variable-compression engine in a quiet room when the engine is under full load, the engine speed is 600 r.p.m., the jacket-water boiling, no external heat applied to the air-hydrocarbon mixture, and the spark timing set for maximum power. This "critical compression ratio" is somewhat similar to Ricardo's "highest useful compression ratio" except that Ricardo used an engine speed of 1500 r.p.m.

Table 74. Detonation Properties and Lead Susceptibility of Hydrocarbons.

Compound	Critical Compression Ratio	Increase in Critical Compression Ratio for Addition of 1 cc. of Tetraethyl Lead per Gallon
<i>Paraffin Hydrocarbons</i>		
Methane	>15	...
Ethane	14	...
Propane	12	...
Isobutane	8.9	...
<i>n</i> -Butane	6.4	...
<i>n</i> -Pentane	3.8	0.50
2-Methylbutane	5.7	0.95
<i>n</i> -Hexane	3.3	0.20
<i>n</i> -Heptane	2.8	0.20
3-Ethylpentane	3.9	0.20
2,4-Dimethylpentane	5.0	0.80
2,2,4-Trimethylpentane	7.7	2.10
2,7-Dimethyloctane	3.3	0.20
3,4-Diethylhexane	3.9	0.30
<i>Unsaturated Aliphatic Hydrocarbons</i>		
Acetylene	4.6	...
Ethylene	8.5	...
Propene	8.4	...
1-Pentene	5.8	0.30
2-Pentene	7.0	0.50
2-Methyl-2-butene	7.0	0.70
Dimethylbutadiene	8.6	0.10
2,4-Hexadiene	6.6	0.10
1,5-Hexadiene	4.8	0.25
1-Heptyne	4.9	0.33
3-Heptyne	3.4	0.10
1-Heptene	3.7	0.25
3-Heptene	4.9	0.80
3-Ethyl-2-pentene	6.6	0.50
2,4-Dimethyl-2-pentene	8.8	0.70
2-Methyl-5-hexene	4.7	0.25
3-Methyl-5-hexene	5.0	0.20
2-Octyne	4.0	0.10
1-Octene	3.4	0.15
2,2,4-Trimethyl-3-pentene	10.0	0.35
2,2,4-Trimethyl-4-pentene	11.3	0.25
<i>Naphthene Hydrocarbons</i>		
Cyclopentane	10.8	2.70
Cyclohexane	4.5	0.65
Methylcyclohexane	4.6	0.30
Cyclohexylacetylene	4.6	0.21
1,2-Dimethylcyclohexane	5.1	0.35
1,3-Dimethylcyclohexane	4.4	0.21
1,2-Methylethylcyclohexane	4.3	0.16
1,3-Methylethylcyclohexane	3.8	0.12
1,4-Methylethylcyclohexane	3.7	0.13
1,2-Methyl- <i>n</i> -propylcyclohexane	3.6	0.12
1,3-Methyl- <i>n</i> -propylcyclohexane	3.4	0.12
1,4-Methyl- <i>n</i> -propylcyclohexane	3.3	0.12
1,4-Methylisopropylcyclohexane	4.0	0.26
1,2-Methyl- <i>n</i> -butylcyclohexane	3.4	0.10

Table 74.—(Continued)

Compound	Critical Compression Ratio	Increase in Critical Compression Ratio for Addition of 1 cc. of Tetraethyl Lead per Gallon
1,3-Methyl- <i>n</i> -butylcyclohexane	3.3	0.10
1,4-Methyl- <i>n</i> -butylcyclohexane	3.2	0.10
1,2-Methyl- <i>n</i> -amylcyclohexane	3.2	0.10
Decahydronaphthalene	3.6	0.13
<i>Aromatic Hydrocarbons</i>		
Benzene	>15	...
Toluene	13.6	...
Phenylethylene	14.0	...
<i>o</i> -Xylene	9.6	...
<i>m</i> -Xylene	13.6	...
<i>p</i> -Xylene	14.2	...
Phenylacetylene	12.4	-0.80
Ethylbenzene	10.5	2.00
Benzylacetylene	7.4	0.12
Methylphenylacetylene	11.8	-0.30
1,4-Methylisopropylbenzene	11.1	1.00
1-Phenylbutadiene	9.5	0.00
Tert-Amylbenzene	12.1	2.00
Trimethylphenylallene	8.3	-0.20
<i>Unsaturated Cyclic Hydrocarbons</i>		
Cyclopentadiene	10.9	-0.90
Dimethylfulvene	9.2	-0.13
Indene	11.2	-0.10
Dicyclopentadiene	11.0	-0.30
Cyclopentene	7.9	0.20
1,3-Cyclohexadiene	5.9	-0.02
Cyclohexene	4.8	0.20
Dipentene	5.9	0.25

The compression ratio of the engine used in this work could be varied from 3 : 1 to 15 : 1.

The marked differences in the knock tendencies of the hydrocarbons become clear when it is realized that commercial gasolines varying from 50 to 80 octane number occupy the comparatively narrow range of critical compression ratios between 3.6 : 1 and 4.5 : 1.

The critical compression ratio was reproducible to within ± 0.1 of a ratio at compression ratios between 3 : 1 and 5 : 1 and within ± 0.5 of a ratio between 12 : 1 and 15 : 1.

The straight-chain paraffins, except those of lowest molecular weight, have the lowest octane numbers, and the tendency to knock rapidly increases with the length of the chain. The knock tendency of the molecules of any hydrocarbon series increases with the size of the molecule.

Normal heptane has a critical compression ratio of 2.8, and its octane value is arbitrarily taken as zero. All straight-chain paraffins of higher molecular weight than heptane have negative octane numbers and begin to knock at or below the critical compression ratio of 2.8.

The branched paraffin molecules, as opposed to the straight-chain paraffins, have higher octane numbers; for example, the octane number of the straight-chain (normal) octane is -17, whereas that of the isoöctane (2,2,4-trimethylpentane) is 100, and that of the still more highly branched octane, the 2,2,3,3-tetramethylbutane, is 103.

Unsaturated compounds usually have higher critical compression ratios than saturated compounds, but there are notable exceptions; ethylene, acetylene, and propene are much lower than the corresponding saturated compounds, acetylene being about 10 ratios lower than the corresponding ethane.

The position of the unsaturated linkage in the molecule affects the critical compression ratio; the ratio usually increases as the double bond is nearer the center of the molecule. However, in the straight-chain heptynes, having a triple, or acetylenic, bond, the critical compression ratio seems to decrease when the triple bond is nearer the middle of the molecule.

Table 75 from some of the earlier experimental work⁵¹ shows the effect on the knock rating of the position of the double bond in the straight-chain olefin molecule. For comparison, the data of the corresponding straight-chain paraffins are also added.

For details of the use of the aniline to measure the knock tendency the reader is referred to the original publication;⁵¹ but the magnitude of the scale may be understood from the facts that (1) normal heptane, which has an aniline equivalent of -14, has an octane number of zero, and (2) isoöctane, which has an aniline equivalent of +16, has an octane number of 100.

Table 75. Aniline Equivalents of Some Straight-Chain Olefins.

Hydrocarbon	Structure	Aniline Equivalent	Aniline Equivalent of Corresponding Paraffin	Increase in Aniline Equivalent Due to Unsaturation
1-Pentene	$C=C-C-C-C$	10	1	9
2-Pentene	$C-C=C-C-C$	16	1	15
1-Hexene	$C=C-C-C-C-C$	8	-6	14
2-Hexene	$C-C=C-C-C-C$	12	-6	18
1-Heptene	$C=C-C-C-C-C-C$	0	-14	14
3-Heptene	$C-C=C-C-C-C-C$	12	-14	26
1-Octene	$C=C-C-C-C-C-C-C$	-8	-21	13
2-Octene	$C-C=C-C-C-C-C-C$	0	-21	21
3-Octene	$C-C=C-C-C-C-C-C$	6	-21	27
4-Octene	$C-C-C-C=C-C-C-C$	12	-21	33

For convenience in showing the molecular structures of the olefins in the table, the hydrogen atoms are omitted.

The investigators examined six of the possible 68 isomers of octene (C_8H_{16}); four are shown in this table. The other two octenes investigated, 2,2,4-trimethyl-4-pentene and 2,2,4-trimethyl-3-pentene, which have

branched structures, showed aniline equivalents of 32 (octane number, 150) and 30 (octane number, 144), respectively. Thus the effect of the branches in the olefins, like that of the paraffins, is to increase the resistance to knock. (*See* octane ratings of Table 77.)

Naphthenes have higher octane numbers than the corresponding aliphatics; long, straight aliphatic side chains lower the knock rating but to a less degree than branched side chains. The introduction of a double bond in the aliphatic side chain or of double bonds in the naphthene ring usually increases the octane number.

Of the commercial hydrocarbons the aromatics, as a class, have the highest octane numbers.

The data of Table 76 show that the critical compression ratio of a mixture of two compounds differing widely in knock tendency is not proportional to the concentration over the whole range of mixture. Such behavior is also observed in the blending together of different fractions of gasoline.

Table 76. Detonation Properties of Two-Component Mixtures.

	Per Cent by Volume	Mole Fraction	Critical Compression Ratio
2,2,4-Trimethylpentane in heptane	0.0	0.0	2.8
	66.0	63.5	4.0
	80.0	77.0	4.6
	100.0	100.0	7.6
Benzene in heptane	0.0	0.0	2.8
	50.0	62.2	3.6
	60.0	71.3	4.0
	70.0	79.2	4.8
	84.0	89.5	7.8
Cyclohexane in heptane	0.0	0.0	2.8
	70.0	76.0	3.8
	80.0	84.0	4.0
	90.0	92.3	4.2
	100.0	100.0	4.5
Benzene in 2,2,4-trimethylpentane	0.0	0.0	7.6
	50.0	65.2	10.2
	75.0	85.0	14.0
Dicyclopentadiene in 2,2,4-trimethylpentane	0.0	0.0	7.6
	10.0	12.1	9.3
	25.0	29.2	10.3
	50.0	55.4	10.8
	100.0	100.0	10.8

Smittenberg, Hoog, Moerbeek, and Zijden⁷¹ have determined the octane values of 50 pure hydrocarbons, including representatives of paraffins, olefins, diolefins, naphthenes, and aromatics. The data are shown in Table 77.

Table 77. Octane Rating of Fifty Pure Hydrocarbons.

Hydrocarbon	B.p. of Sample Used for Octane Rating (°C.)	Octane Number C.F.R.-A.S.T.M. Motor Method	Hydrocarbon	B.p. of Sample Used for Octane Rating (°C.)	Octane Number C.F.R.-A.S.T.M. Motor Method
<i>Paraffins</i>			<i>Olefins</i>		
Methane	-161.6	110	Ethene	-102	81
Ethane	-88.5	104	Propene	-47.7	85
Propane	-42.2	100	<i>n</i> -Pentene (2-pentene)	36.4	80
<i>n</i> -Butane	-0.5	92	<i>n</i> -Hexene (2-hexene)	67.6	78
2-Methylpropane (Isobutane)	-12.2	99	2-Methyl-2-pentene	67.4	78
<i>n</i> -Pentane	36	61	3-Methyl-2-pentene	69.5	79
2-Methylbutane	27.8	89	2,2-Dimethyl-3-butene	41.5	84
Dimethylpropane	9.6	83	2,2,3-Trimethylbutene	77.8	89
<i>n</i> -Hexane	68.8	25	<i>n</i> -Octene (2-octene)	124.6	55
2-Methylpentane	60.3	73	3-Methyl-2-heptene	122	74
3-Methylpentane	63.2	75	2,4,4-Trimethyl-1- and 2-pentene (mixed isomers)	100	86
2,2-Dimethylbutane	49.7	96			
2,3-Dimethylbutane	58.1	95	<i>Diolefin</i>		
<i>n</i> -Heptane	98.4	0	2,4-Hexadiene	80	77
2-Methylhexane	90.1	45			
2,2-Dimethylpentane	79.3	93	<i>Naphthenes</i>		
2,3-Dimethylpentane	89.8	89	Ethylcyclobutane	70.7	68
2,4-Dimethylpentane	80.6	82	Cyclopentane	49.2	83
3,3-Dimethylpentane	86.1	84	Methylcyclopentane	72	82
2,3,3-Trimethylbutane	81	101	Cyclohexane	80.8	77
<i>n</i> -Octane	125.8	-17	Methylcyclohexane	110.3	71
3-Methylheptane	119.1	35			
2,3-Dimethylhexane	115.8	76	<i>Aromatics</i>		
2,5-Dimethylhexane	109.3	52	Benzene	80.1	108
3,4-Dimethylhexane	117.9	85	Toluene	110.8	104
2,2,3-Trimethylpentane	110.1	102			
2,2,4-Trimethylpentane	99.1	100			
2,3,4-Trimethylpentane	112.8	97			
3-Methyl-3-ethylpentane	118.4	91			
2,2,3,3-Tetramethylbutane	106.5	103			
<i>n</i> -Nonane	150.7	-45			

Lead Susceptibility

The data of Table 74, column 3, show that the pure hydrocarbons vary enormously among themselves in tetraethyl lead susceptibility (1 cc. tetraethyl lead per gallon), the effect depending on their molecular structure and other properties. The response of gasolines to one cc. of tetraethyl lead per gallon varies from 0.1 to 0.3 on the scale used in Table 74, whereas the response of the individual hydrocarbons varies from -0.9 for cyclopentadiene, as the lowest, to 2.7 for cyclopentane, as the highest.

In a few rare instances the one cc. of tetraethyl lead per gallon actually increased the knock tendency (*e.g.*, the cyclopentadiene). Of the compounds reported in Table 74, a branched paraffin (2,2,4-trimethylpentane), a naphthene (cyclopentane), and a benzene with a saturated side chain (ethylbenzene) possessed the greatest lead susceptibilities, the one cc. per gallon increasing the permissible compression ratio by more than two points.

In the different classes of hydrocarbons the lead susceptibility is greatest in the aliphatic and naphthenic hydrocarbons and least in the unsaturated cyclic hydrocarbons. The order of the response to lead is as follows, those most susceptible being given first:

- (1) paraffins and naphthenes;
- (2) aromatics having a saturated side chain;
- (3) olefins and diolefins;
- (4) unsaturated cyclic compounds.

It is observed that the classes of hydrocarbons having the greatest tendency to knock are the most favorably influenced by tetraethyl lead.

In a broad generalization of the lead susceptibility of the aliphatic double- and triple-bonded compounds, it is observed that the double-bonded compounds give higher response to the lead than the triple-bonded compounds, and give highest response when the position of the double bond is elsewhere than at the end of the molecule. In the straight-chain olefins the effectiveness of the lead is greater, the nearer the double bond is to the center of the molecule.

The most responsive of the benzene ring compounds appear to be those that also contain a saturated side chain. An olefinic unsaturation in the side chain lowers the susceptibility, and a triple bond in the side chain renders the response negative to the lead.

In the three cyclic compounds, cyclohexane, cyclohexene, and cyclohexadiene, the effect of the lead becomes progressively less with the degree of unsaturation until the cyclohexadiene is negative.

Detonation Characteristics of Gasolines

The practical method of preparing high octane motor fuels usually consists in producing the gasoline itself with the highest octane value consistent with economy and then adding tetraethyl lead.

The gasolines now sold as automobile fuels by almost all the major refiners are blended products, which usually comprise natural gasoline, straight-run and "reformed" straight-run gasoline, cracked gasoline, polymerized gasoline, and alkylated gasoline. Cracked gasoline has a higher octane number than straight-run gasoline from the same fuel because of its higher content of olefins, isomeric paraffins, and cyclic compounds.

The gasolines cracked in the vapor phase (and at higher temperatures) have still more resistance to knocking than those cracked in the liquid phase. The percentage of unsaturated compounds in vapor phase-cracked fuel is higher than in liquid phase-cracked fuel. Stock cracked at higher temperatures yields gasoline with higher antiknock properties and usually with lower sulfur content, and, as noted in a preceding chapter, the removal of the sulfur may not appreciably improve the octane number of the gasoline *per se*, but the removal improves the lead susceptibility of the gasoline.

Straight-run gasolines of low octane number and heavy (high-boiling) naphthas, whether straight-run or cracked, and often light kerosenes may be subjected to reforming, or cracking, so as to alter the nature of the hydrocarbons and yield higher antiknock properties. For the reforming, high temperatures (950 to 1050° F.) and high pressures (250 to 1000 pounds) are commonly used, and the time of exposure of the hydrocarbons to the heat is short (10 to 20 seconds). The yield of product is usually around 75 to 90 per cent; it depends on the degree of cracking required. The resulting rise in the octane number varies from 15 to 35 points. A study of the effects of varying the conditions of reforming on the yields and nature of the products has been reported by Turner and Le Roi.⁷⁸

The reforming increases the amount of low molecular weight hydrocarbons in the fuel and produces changes in the molecules themselves, thus: the original gasoline consisting of paraffins and naphthenes is converted into a gasoline relatively rich in olefins and naphthenic and aromatic cyclic compounds. Apparently very little isomerization (rearrangement of the atoms within the molecules to yield branched-chain compounds) occurs at the reforming temperatures, although such isomerization by the aid of catalysts²⁰ is possible with pure straight-chain compounds. However, our present information on isomerization with the aid of catalysts is limited to the lower molecular weight paraffins, such as butane and pentane. The potential value of isomerization is illustrated in the two octanes, the straight-chain octane and the isoöctane (2,2,4-trimethylpentane) with octane numbers of -17 and +100, respectively.

Other methods of producing high octane hydrocarbons now used on a large scale as blending agents consist in:

(1) Isolating almost pure isopentane from natural gasoline. The natural gasoline usually contains about 10 to 15 per cent isopentane (octane number of pure isopentane is 90);

(2) Isolating a central fraction, the heart cut, of natural gasoline,¹⁷ octane number, 71-75;

(3) Polymerizing or uniting two low molecular weight olefin molecules thermally, or more commonly catalytically, as with phosphoric acid at

moderately high temperatures. The product is an unsaturated compound, an olefin, and contains one double bond;

(4) Combining (alkylating) a low molecular weight branched-chain paraffin, especially isobutane, with a low molecular weight olefin, especially ethylene, propene, and butene (straight-chain or branched-chain butene). The alkylation product has no unsaturated linkages and is thus paraffinic.

When the branched-chain butene is alkylated with isobutane, the product is practically pure isoöctane. Isoöctane is also made on a large scale by the polymerization of isobutene to diisobutene and then the hydrogenation of the diisobutene to isoöctane. For details of the commercial manufacture of isoöctane the reader is referred to McAllister,⁵³ Coulthurst,⁵⁰ Hubner and Egloff,⁵⁰ Birch *et al.*,⁵ Egloff,⁵² Egloff, Morrell, and Nelson,⁵⁴ and Gard, Blount, and Korpi.⁵⁵ The Phillips Petroleum Company⁵² is now manufacturing neohexane by alkylating ethylene with isobutane.

(5) Producing isopropyl ether commercially from refinery stabilizer gas, consisting of a mixture of propene and propane. Under the catalyzing influence of sulfuric acid the propene gas reacts to form the isopropyl ether, $(\text{CH}_3)_2\text{CH} \cdot \text{O} \cdot \text{CH}(\text{CH}_3)_2$; boiling point, 154-156° F.; Reid vapor pressure, 5 pounds per sq. in.; and octane number, 98.

Aromatic constituents extracted by the Edeleanu process from petroleum products, especially when properly fractionated, or first cracked and then fractionated, have high antiknock properties.⁵⁷ Terpenes, monoethylbenzene, or other alkyl benzenes in which the alkyl side chain, or chains, has at least two carbon atoms (such as propyl, isopropyl, butyl, or mixed derivatives),⁵⁸ and products of the destructive hydrogenation of brown coal have high antiknock values.⁴²

High Octane Number Aviation Fuels

Cracked and reformed gasolines are not accepted as aircraft fuels, because of their chemical instability and tendency to form gums. Much of the commercial aviation gasoline of 73-74 octane number is straight-run naphtha of proper volatility from naphthene-type crude oil and natural gasoline, to which tetraethyl lead has been added.

The refinery products suitable for the especially high octane number aircraft fuels are alkylation gasolines, isopentane, narrow fractions (heart cuts) from natural gasoline, neohexane, and isopropyl ether. These products are all highly susceptible to tetraethyl lead.

The use of the foregoing products is illustrated by a blend of 60 per cent of the heart cut of natural gasoline and 40 per cent of isoöctane; this blend has an octane number of 82 to 84, which increases to 100 with 3 cc. of tetraethyl lead per gallon. A blend of commercial isoöctane and 30 per cent of a heart cut of natural gasoline (octane number about 75) has an octane number of about 92, which increases to 100 with only 0.5 to 1 cc. of tetraethyl lead per gallon; the use of 3 to 6 cc. of tetraethyl lead per gallon would give it a value equivalent to about 110 octane.

At present no commercial fuels having boiling points satisfactory for proper carburetion have fully 100 octane number without the addition of lead. The nearest approaches to 100-octane fuels are such blends as (1) 5 per cent isopentane, 5 per cent neohexane, and 90 per cent isoöctane, or (2) 10 per cent of either isopentane or neohexane with 90 per cent isoöctane. These blends have octane numbers of 99 to 99.4, which are increased to an equivalent of about 115 by the addition of 3 cc. tetraethyl lead per gallon.

Test Methods of Determining Octane Numbers

Several methods exist for determining the detonation characteristics of motor fuels, as shown in Table 78.

Table 78. Common Methods of Determining Octane Numbers.

Method	Engine Speed (r.p.m.)	Cooling Jacket (°F.)	Intake (°F.)	Type of Knock Indicator
A.S.T.M. Motor	900	212	300	a
British Air Ministry	900	212	260	a
Low Temperature	900	212	No Preheating	a
L-3	900	212	260	a
C.F.R. Research	600	212	No Preheating	a
U. S. Army Air Corps	1200	330	Not Measured	b

^a Bouncing pin and knockmeter.

^b Temperature plug and potentiometer.

In this country two methods are in extensive use; the A. S. T. M. Motor Method (frequently designated, A. S. T. M.-C. F. R. Motor Method), and the C. F. R. Research Method (commonly designated, 1937 C. F. R. Research Method). The L-3 method was used by the Ethyl Corporation until May 15, 1940, and then abandoned. Details of the A. S. T. M. Motor method in its present form may be found in the current (1941) A. S. T. M. Standards on Petroleum Products and Lubricants, Designation: D357-41T.

The octane rating is necessarily made under very arbitrary conditions. Investigators in extensive experiments have endeavored to make the test anticipate as closely as possible the actual performance of the gasoline in service.* Complete correlation is not now considered possible. Under the present development of octane rating, the gasoline may show in actual use, in extreme cases, a performance equivalent to ten octane units higher or seven units lower than that of the A. S. T. M. laboratory method, which correlates more closely with road tests than the others.

There are many causes for the variation between laboratory and road

* For reproducibility of octane numbers in the laboratory the literature should be consulted.¹²

tests and general performance in actual use. These causes have been discussed in the literature.⁶⁷ Illustrative of the differences in knock rating induced by operating under different conditions are the data of Cramer and Campbell²¹ obtained from testing two pure hydrocarbons at different engine speeds, as shown in Table 79.

Table 79. Comparative Effects of Different Engine Speeds on the Relative Knocking Characteristics of Isodecane and Isooctane.

Engine Speed (r.p.m.)	Critical Compression Ratio	
	Isodecane	Isooctane
600	11.3	7.7
1000	11.6	8.3
1500	11.6	...
2000	11.5	12.0

At 600 r.p.m. under the conditions of the test, isodecane is considerably higher in antiknock value than isooctane. As the speed increases, isodecane does not change appreciably in antiknock property, but isooctane increases rapidly, so that at 2000 r.p.m. it has appreciably greater resistance to knock than isodecane.

Although gasolines do not have such great variations as the two individual hydrocarbons just noted, nevertheless the averages of their chemical composition are sufficiently different to cause great irregularities in different methods of test. Some of the causes of the differences in laboratory tests and road performance are the conditions and adjustments of the motor on the road and the manner in which it is operated. Some of these differences are reviewed below.

(1) **Spark timing and distributor adjustment.**^{5, 36} Tests show that a difference of one degree in the basic spark setting affects detonation by an equivalent of 1.6 to 2.0 octane numbers. When in perfect condition, the automatic spark mechanism of an automobile is accurate to plus or minus 2°, which is equivalent to 6.4 up to 8.0 octane numbers in the gasoline—an average difference between regular and premium-grade gasolines. After an automobile is used for an appreciable time, the mechanism usually functions less accurately. The electrical distributing system, especially when worn, may cause very uneven timing in the cylinders and produce very different octane number requirements for the different cylinders.⁵

Van Hartesveldt and Field⁸⁰ report that in the work done by the Atlantic Refining Company in the 1939 C. F. R. motor survey, five cars were chosen as having abnormal octane requirements. The cars were tested for octane requirements and power output at speeds of 20, 35, and 50 miles per hour before and after proper adjustment of the distributor system. The results are shown in Table 80.

Table 80. Effect of Distributor Adjustment on Octane Requirement and Power.

Car	—Before Distributor Adjustment—		—After Distributor Adjustment—	
	Octane Requirement	Average Rear-Wheel Horsepower; 20, 35, and 50 Miles per Hour	Octane Requirement	Average Rear-Wheel Horsepower; 20, 35, and 50 Miles per Hour
1938 A	83.3	27.6	78.5	28.4
1938 B	59.8	24.4	56.4	25.8
1937 C	80.6	23.2	78.6	26.3
1938 C	83.1	26.2	71.4	28.8
1939 C	76.4	36.9	74.4	37.6
Average	76.6	27.6	71.9	29.4

The distributor adjustments lowered the average octane requirements by 4.7 numbers and increased the power output by 6.5 per cent.

Corresponding malfunctioning of the electric distributor systems of automobiles was observed in a special investigation by fourteen organizations, including major oil and automobile companies, in the annual C. F. R. motor survey of 23 models of the 1939 cars.^{11, 80} By adjustment of the distributors in the manner intended by the manufacturers, the average requirement in sixty per cent of the cars was lowered by 6 octane numbers.

(2) **Fuel distribution.** The higher-boiling fractions of the gasoline tend to drop out of the air-fuel mixture in the average manifold. The droplets accumulate in the manifold but eventually get into one or more of the cylinders, and fuels of varying composition reach the different cylinders. This condition is especially common at low speeds.^{5, 7} The octane requirements thus vary in different cylinders, and are dictated by the worst cylinder.

(3) **Carbon deposits in the engine.** The accumulation of carbon in the cylinder head rapidly makes higher octane fuel necessary; in careful measurements in two different motors under what was considered average conditions, the octane requirement increased 7 points in 12,500 miles.¹³ Other changes in the engines during the 12,500 miles increased the total octane requirement by about 25 units. To operate the motors at the end of the 12,500 miles on the same octane requirement as at the beginning, it was necessary to retard the spark by 9 crankshaft degrees—about one degree per 1400 miles of driving.

(4) **Vapor losses.** Under adverse conditions in an automobile, as much as four per cent of the most volatile and highest antiknock constituents of the gasoline may be vented from the rear tank and carburetor, a condition rendering the gasoline performance much poorer than indicated by the laboratory octane rating.

(5) **Humidity.** Air humidity has an appreciable influence on the detonation of gasoline. MacGregor⁵⁴ has shown experimentally the influence of moisture in the air on the suppression of detonation. When the humidity of the air was raised from 0.002 to 0.023 pound of water per pound of dry air (equivalent to a change in water-vapor pressure of one

inch of mercury), the octane number increase in the fuels was as follows: octane-heptane mixture, 5.1; straight-run gasoline, 7.2; straight-run gasoline with tetraethyl lead, 10.8; and cracked gasoline, 7.9.

Studies have been made of the possibility of recovering part of the water from the exhaust of airplane engines for injection into the intake manifolds with the gasoline (a gallon of gasoline when consumed produces considerably more than a gallon of water).

Other factors as important as the preceding in causing variations in the performance of fuels are: the design of the motor,⁴⁰ temperature of air-fuel mixture and engine cooling water,^{64, 70} carburetor setting (associated with manifold distribution, air-fuel mixture, and fuel characteristics), compression ratio, volumetric efficiency, altitude, etc.

Van Voorhis⁸¹ points out that the principal problem of the Motor Fuels Division of the Cooperative Fuel Research Committee for 1940 is the correlation of road and laboratory tests.

Estimating Octane Value of Motor Fuel from Chemical and Physical Data

Because it is known that the physical characteristics and chemical constitution of the hydrocarbons influence the octane rating, attempts have been made to calculate the octane numbers of fuels; so far as chemical knowledge extends, a fairly high degree of correlation between the calculated and the experimental data is found. An extensive study of the correlation has been made by Schneider and Stanton⁶⁸ and by Smith.⁷⁰ It appears that such a method has very limited practical application, although it is of some significance in evaluating the octane numbers of stocks from the same source and for anticipated synthetic compounds.

Methods of Suppressing the Detonation of Gasolines

The detonation characteristics of the pure hydrocarbons and of the different types of gasolines have already been noted.

The shape of the cylinders, the composition of the metal of which they are made, the general design of the engine, etc., greatly influence the tendency of the fuel to knock.

A very small amount of a material, such as tetraethyl lead, can be added to the fuel as a catalyst to lessen or prevent the detonation (these substances are the true antiknock reagents of the trade). The influence of these substances will be considered.

Small Amounts of Antidetonants, or Catalysts

Though the addition of very small quantities of many different substances for the suppression of detonation has been proposed, only tetraethyl lead

and, to a limited extent, aniline and iron carbonyl, have found practical application. They are described briefly below. The relatively high efficiency of tetraethyl lead as a knock inhibitor is shown in Table 81. These data were developed by Midgley and Boyd⁵⁸ from the compilation of the relative effects of a number of compounds in comparison with benzene for suppressing the detonation of kerosene in a motor.

Table 81. Comparison of a Few Efficient Antidetonants with Benzene.

Compound	Per Cent by Volume in Kerosene Re- quired to Effect a Given Suppression of Detonation	Number of Gram Molecules in a 355 Cc. Mixture with Kerosene to Give Equal Suppression of Detonation
Benzene	25.0	1.0
C ₂ H ₅ I	1.6	0.07
Xylidine	2.0	0.059
(C ₂ H ₅) ₄ Sn	1.2	0.021
(C ₂ H ₅) ₂ Se	0.4	0.013
(C ₂ H ₅) ₂ Te	0.1	0.003
(C ₂ H ₅) ₄ Pb (tetraethyl lead)	0.04	0.0007

Many substances have been patented as antidetonants, but the efficiency of most of them is low or negligible; consequently the cost of the best of these is too great for the large volume required to achieve knock suppression equivalent to that of tetraethyl lead. It is of interest to know that the United States Bureau of Standards early made tests on 150 such gasoline dopes for which extensive claims of antidetonating properties were made; but in the proportions specified, no measurable effect could be found in any one of them. These tests did not, of course, include tetraethyl lead and other knock suppressors of generally known value.²⁵

The patents described briefly below pertain to substances possessing some property as suppressors of detonation when used in sufficiently large amounts. The list may be of some value to those especially interested in such developments: 0.1 to 1.0 per cent iron acetyl acetone in gasoline,⁵⁹ tin tetramethyl, lead tetramethyl, and selenium diethyl;⁶⁰ 0.2 to 0.5 per cent hydroquinone (para-dihydroxybenzene),⁶² organic and inorganic metal salts supposed to render gasoline electrically conducting (lead nitrate, copper nitrate, metallic phenates, cresolates, and carbonates, bismuth tri-phenyl, etc., first dissolved in liquids miscible with the fuel),⁶³ dianinomesitylene,⁶ iodine and iodine compounds [methyl, ethyl, propyl, phenyl iodides, iodoform, tin tetraiodide, lead diethyl or lead diphenyl iodide,¹⁷ iodine compounds which are unstable in the conditions existing in the motor cylinder, such as iodoaniline or iodides or polyiodides of tetraethylammonium (1:500 or less)],⁶⁴ aniline and nitrobenzene,^{6,74} thallium or thallium oxide, vaporized outside the cylinder and injected into the cylinder, or about 0.2 per cent of thallium benzylate, oleate, amyl alcoholate, or ethyl acetoacetate;⁶⁵ 0.3 to 0.5 per cent of esters of high molecular weight fatty acids (oleic, palmitic, myristic, or lauric), or corresponding aldehydes, ketones, lactones, anhydrides of acids, or their derivatives treated with halogens, oxygen, or ozone,³ potassium gallate, oxalate, or citrate, their solutions or dispersions in liquids not miscible with the fuel, in which case emulsifying agents are added;⁴⁹ 0.5 to 1.5 per cent potassium oleate or naphthenate, or, in general, compounds of an alkali metal which can be made

miscible with gasoline (oleate, naphthenate, or sulfonate),³⁰ heavy metal derivatives of a beta-diketone (iron, nickel, cobalt, chromium, thorium, copper, and the other heavy metals), aluminum or zinc compounds of acetyl-acetone, benzoylacetone, and their alkyl or aryl homologs,³¹ metallic colloids dispersed in gasoline,³² the value of which is, however, questioned,³³ nickel carbonyl,³⁴ metal aminocarbonyl compounds (iron diethylaminopentacarbonyl),³⁵ antimony trichloride (18 grams per gallon),³⁶ triphenylmethyl derivatives, diphenylnitrosoamine, or polyphenyl ethanes, polyphenyl derivatives of hydroquinones, amines, hydrazines, etc. Amines, organic halogen compounds, esters, tetraethyl silicon, tricresyl phosphate, zinc oleate or isovalerate, aluminum palmitate, compounds of acetoacetic ester with aluminum, magnesium, or iron, calcium naphthenate, and similar compounds in combination with iron carbonyl are also patented.³³

Some nitrogen compounds suppress detonation (primary and secondary amines); some increase it (propyl nitrite); and others are indifferent (pyridine).¹⁰ Methyl aniline suppresses detonation, but dimethyl aniline is inert. Toluidines and xylydines suppress detonation, and they decrease in efficiency from meta- to ortho- and to para-compounds.³⁵ Among oxygen compounds ether increases detonation, alcohols suppress it.³⁰ Carbon disulfide suppresses detonation.^{35, 74}

Tetraethyl lead, other derivatives of lead, such as the alkyl and phenyl compounds, methyl, isopropyl, and triethyl hydroxyl compounds of lead, and lead acetate or oleate, and the alkyl compounds of selenium, tellurium, tin, arsenic, antimony, and other metals of groups 4, 5, and 6 of Mendeleev's table are included in the early Midgley patents.⁵⁷ Iron carbonyl,⁶⁰ mixtures of iron carbonyl and tetraethyl lead or nickel carbonyl,⁴¹ and iron carbonyl and an organic halogen compound (halomethane or halobenzene)⁴⁴ are specified in patents. It is of interest to note that although compounds of quadrivalent lead show antidetonating properties, those of bivalent lead, with a few exceptions, do not show these properties. Lead diphenyl dintrate, tin bromide, iron chloride, aluminum triethyl and aluminum chloride, and bismuth triphenyl dichloride have no antidetonating properties.³⁷

Anilol

Certain substances have been found suitable for use as antidetonants if they and the fuel are separately fed into the motor, but this type does not yet have broad application;² aniline in alcohol, or "Anilol,"* is the best representative of these substances.

Anilol is a blend of aniline and alcohol (butyl alcohol mixed with either ethyl or methyl alcohol) which is injected into the carburetor in controlled quantity to prevent knocking in the motor.⁷⁶ For convenience the Anilol injection valve can be actuated by the throttle to give an automatic supply or increase the supply as needed. As much as six per cent by volume can easily be added by the injection method. A gasoline can be selected that will detonate only during acceleration or at slow speed on hills. At such times, wider opening of the throttle supplies the needed Anilol. Such operation supplies the antiknock material only when it is needed. Obviously,

* Developed by L. H. Kimball of the Fuel Development Company.

there is never anything gained by adding a knock suppressor when there is no knock. Likewise, high antiknock fuels do not increase the power output in a non-knocking engine.

The effect on the knock rating and the lead susceptibility of gasoline of the addition of 2 per cent by volume of Anilol, aniline, and alcohol, respectively, is shown in Table 82, by Hubner and Egloff.⁸⁹

Table 82. Comparative Effects of "Anilol," Aniline, and Alcohol on Detonation and Lead Susceptibility.

	Non-Leaded	+1 cc. TEL/gal.	+3 cc. TEL/gal.
Straight-run gasoline*	70	79	84
With 2% Anilol	76	83	86
With 2% aniline	78	85	88
With 2% alcohol (ethyl)	71	80	85
Blend isoöctane and straight-run gasoline*	87	95	100+
With 2% Anilol	90	97	100+
With 2% aniline	91	98	100+
With 2% alcohol (ethyl)	88	96	100+

* 70 octane number.

Iron Carbonyl

Iron carbonyl⁶⁰ is about 40 per cent as efficient as tetraethyl lead in suppressing detonation, but it rapidly decomposes in light and gives some trouble in short-circuiting spark plugs by depositing magnetic iron oxide (Fe_3O_4) on the porcelain insulator. Iron carbonyl is inexpensive and has been manufactured and used commercially, principally in Germany.

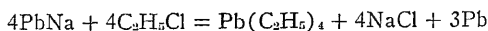
Tetraethyl Lead

Tetraethyl lead has proved thus far the most practical of the catalysts for suppressing detonation; it is manufactured and used on a large scale.⁵⁷ Gasoline containing tetraethyl lead was first put on sale in Dayton, Ohio, February 1, 1923. Because of the poisonous character of tetraethyl lead, many fatalities occurred during its first method of manufacture, but trustworthy investigation showed that with proper precautions it can be handled without danger.

The amount of tetraethyl lead used in gasoline is from 0.75 to 3 cc. per gallon; the maximum amount legally permissible for automobiles is 3 cc. per gallon, although more may be used in aviation gasolines.

The influence of tetraethyl lead in suppressing knocking is not proportional to the amount added, the first cubic centimeters per gallon added being more effective than succeeding additions. In this respect it is different from aromatic compounds. This effect does not, however, seriously affect its commercial application, since only a few cubic centimeters of the fluid per gallon are used.

Tetraethyl lead is now manufactured by reacting ethyl chloride with an alloy of metallic sodium and lead at moderate temperatures and pressures. The equation representing the essential reaction is:



At the completion of the reaction, the tetraethyl lead is distilled with the aid of steam from the other products. Tetraethyl lead is a colorless, oily liquid with a sweetish odor; its boiling point is 392° F. (200° C.), and specific gravity, 1.62.

In addition to tetraethyl lead, the finished ethyl fluid contains ethylene dibromide, ethylene dichloride, and dye; but since the antiknock value is due to the tetraethyl lead only, the concentrations in the finished gasoline are always expressed in terms of the tetraethyl lead rather than the ethyl fluid.

The manufacturers of the ethyl fluid have made minor changes in the product since it was first marketed. One recent analysis of the fluid is shown in Table 83.

Table 83. Ethyl Fluid Composition.

	%
Tetraethyl lead	63.30
Ethylene dibromide	25.74
Ethylene dichloride	8.73
Dye and impurities	2.23

Ethylene dibromide is added to the fluid to furnish halogens to combine with the lead to form volatile lead bromide during the combustion process. The lead bromide is swept out of the cylinders in the exhaust gases.

The deposits on the piston head and cylinder walls of an engine using leaded fuels consist of lead bromide, lead sulfate, metallic lead, and lead oxides. The composition of the deposit varies with the sulfur content of the fuel, the operating temperature of the engine, and other conditions.

Banks⁴ has noted that the corrosiveness of the exhaust gases of leaded fuels to the muffler and associated parts during idling and starting periods is caused by lead oxybromide and condensed water. (Such parts are also corroded during the same periods by a fuel rich in sulfur, such as one with about 0.2 per cent or more sulfur.)

Calingaert and Gambrill¹⁴ have described a convenient and accurate method for the quantitative determination of the tetraethyl lead in any kind of gasoline, including cracked gasolines that may contain alcohol. The gasoline is refluxed with concentrated hydrochloric acid until all the lead is converted into lead chloride. The lead chloride is then extracted from the gasoline with water, and the lead determined quantitatively by any standard method. The method was thoroughly tested by the Ethyl Gasoline Corporation on widely different types of gasoline. It was also tested by fourteen laboratories on six samples of gasoline made from three different base stocks. The method yields results within a mean error of only -0.012 cc.

of tetraethyl lead per gallon of gasoline. The precision is greater than that of the bromine method.⁷⁹

Edgar⁷⁸ describes a plant at Baton Rouge, La., for the manufacture of tetraethyl lead, which has an annual capacity of over 60,000,000 pounds of tetraethyl lead.

Midgley⁷⁶ reviews the history of the discovery and early development of tetraethyl lead as a knock inhibitor.

The Ethyl Gasoline Corporation has rigorously maintained a high standard in the quality of all gasoline sold as Ethyl gasoline. The gasoline must have proper volatility to meet certain specifications; its knock rating must be equivalent to or greater than 80 octane; the gum content must be sufficiently low not to interfere with the function of the tetraethyl lead; the gasoline must not be corrosive, but no limitation is now made on the total sulfur content, whereas it formerly was 0.1 per cent.

Non-detonation Catalysts Fixed on the Inside of the Motor

Painting the inside of the explosion chamber of the cylinders with substances which give reversible chemical reactions of the type that are endothermic at high temperatures and exothermic at low temperatures has been proposed. Mardles⁵⁵ has recently discussed the influence of surfaces in this connection and gives several references to the various investigations. Carbonates of lead, copper, calcium, magnesium, sodium, or potassium, mixed with an inert material, such as silica, and antimony, tellurium, and other metals (except zinc) having a melting point between 575 and 1300° F. have been patented.⁷³ Oxides of vanadium, cobalt, and rare-earth metals, particularly cerium, have also been recommended, such compounds being known to the trade as "Katalite."⁷² However, because of fouling and other mechanical difficulties, as well as low efficiency in accomplishing its purpose, but little is expected from the innovation.

Influence of Inhibitors on Preserving Antidetonaⁿt Qualities of Gasoline

Egloff, Faragher, and Morrell³³ early reported an investigation on the influence of small quantities of material in preventing loss of antidetonating properties of cracked gasoline in storage. They observed that some samples of cracked gasolines kept in storage for several months lose as much as 65 per cent of the original benzene equivalent, but other samples undergo practically no change. The cause of the difference is not definitely known, but the behavior is influenced by the character of the charging stock and the conditions of cracking. The data of Table 84 show the change in knock rating of a number of these cracked gasolines.

The A. P. I. gravities of the 10 samples listed in Table 84 were between 58.4 and 62.3, and the initial boiling points were between 100 and 113° F.

Table 84. Knock Rating of Cracked Gasolines Before and After Storage.

Months in Storage	Metal Container (Tin or Iron) Condition after Storage	Source of Gasoline	E.B.P. °F.	Benzene Equivalent Before Storage	Benzene Equivalent After Storage
6	Clean	Smackover	419	45	45
11	Red Gum Deposit	So. Field, Ark.	367	35	15
11	Slight Deposit	So. Field, Ark.	388	32	30
12	Clean	Mid-Continent	389	37	38
12	Clean	Mid-Continent	391	37	34
12	Clean	Mid-Continent	391	35	20
12	Clean	Mid-Continent	402	37	12
23	Clean	Mid-Continent	377	40	31
23	Clean	Mid-Continent	422	42	32
23	Clean	Mid-Continent	400	45	36

Since cracked gasolines form oxidation products on standing, some of which are gum-forming substances, Egloff, Faragher, and Morrell investigated the influence of certain antioxidation catalysts on inhibiting the formation of gum and the loss in knock rating. Aniline, hydroquinone, naphthalene, and anthracene were found to be effective inhibitors. The same substances were also effective in preventing a reduction in knock rating in gasolines subjected to accelerated oxidation¹ by heating the gasoline to a temperature of 212° F. in an atmosphere of oxygen for five hours.

The accelerated oxidation test in experiments using a Pennsylvania cracked gasoline lowered the benzene equivalent from 40 to 29 per cent, but the addition of 0.1 per cent by weight of aniline or hydroquinone preserved the knock rating.

Table 85. Chemical Inhibitors in Accelerated Oxidation Tests.

Pennsylvania Cracked Gasoline

	Without Inhibitor		With 0.1% Inhibitor and Accelerated Oxidation					
	Original Gasoline	After Oxidation	Aniline	Hydroquinone	Urea	Phenol	Naphthalene	Anthracene
I.B.P. (°F.)	94	114	112	105	130	114	108	122
E.B.P. (°F.)	427	434	429	430	431	432	434	445
Color Saybolt	24	-16	-16	Yellow	-5	Yellow	0	-2
Mgs. gum, copper dish	19	220	55	16	56	139	241	75
Mgs. gum, glass dish	3	55	5	6	14	36	36	20
Benzene equivalent, % (Delco motor)	40	29	39	40	34	31	35	34

Mid-Continent Cracked Gasoline

I.B.P. (°F.)	103	114	106	110	108	107	108	118
E.B.P. (°F.)	320	335	319	313	301	302	313	312
Color Saybolt	30	7	-16	13	26	16	28	28
Mgs. gum, copper dish	68	475	389	26	198	131	126	73
Mgs. gum, glass dish	1	136	29	3	13	16	5	3
Benzene equivalent, % (Delco motor)	56	37	34	52	40	47	47	47

The data of Table 85, show the detailed experimental results, and the data of Table 86 pertain to a Mid-Continent cracked gasoline of 410° F. end point with its octane rating completely stabilized by the inhibitors.

Table 86. Mid-Continent Cracked Gasoline and Chemical Inhibitors.

	Saybolt Color Before Oxidation	Saybolt Color After Oxidation	Gums Mg. Per 100 Cc. Copper Dish	Benzene Equivalent Per Cent (Delco Motor)
Gasoline alone				
Before oxidation	20		25	32
After oxidation	..	Yellow	331	15
Gasoline + 0.1% inhibitor				
Aniline	Yellow	Yellow	9	36
Dimethylaniline	16	Yellow	22	30
Diethylamine	16	Yellow	337	30
Hydroquinone	20	Yellow	11	31
Anthracene	18	Yellow	60	30

Aniline is a stabilizer and also has antiknock properties of its own when added to gasoline. The increase of 4 per cent of benzene equivalent is the calculated effect for the quantity of aniline added.

These investigators subjected cracked gasoline from different sources to accelerated oxidation; the loss in the antiknock values is recorded in Table 87.

Table 87. Changes in Knock Rating with Accelerated Oxidation.

Gasoline	I.B.P. (°F.)	E.B.P. (°F.)	Benzene Equivalent (Per Cent) (Delco Motor)	
			Original Gasoline	Gasoline After Oxidation
California	92	428	55	51
Pennsylvania	94	427	40	29
Mid-Continent	103	320	56	37
Mid-Continent	107	411	36	21

Scheumann⁶⁶ observed the effect of the accelerated oxidation on the octane rating of cracked gasoline with and without inhibitors, as shown in Table 88.

Table 88. Stabilization of Knock Rating.

Inhibitor	Concentration (mg./100 cc.)	Before Oxidation		After Oxidation	
		Actual Gum (mg./100 cc.)	Octane Number	Actual Gum (mg./100 cc.)	Octane Number
None	0.0	1.0	70	184	60
Alpha-Naphthol	1.0	1.0	70	7.3	68
Pyrocatechol	1.0	1.0	70	1.2	69
Inhibitor No. 5	2.0	1.0	70	8.3	64
Inhibitor No. 5	5.0	1.0	70	1.3	69

It has been pointed out³³ that there is apparently some close relation-ship between the depreciation in knock rating and the increase in gum formation. As a rule, those materials which inhibit gum formation also check

depreciation in knock rating, although there are some exceptions to this generalization, *e.g.*, diethylamine inhibits the depreciation of knock rating under the test conditions but does not prevent increase in gum. On the contrary, it appears to promote gum formation. Other substances inhibit knock depreciation but fail to prevent increase in gum.

Egloff, Faragher, and Morrell³³ early found that the original octane value of a cracked gasoline which had depreciated in storage could be restored by retreating the gasoline (*e.g.*, with 3 pounds acid of 75 to 95 per cent concentration, per barrel) and redistilling it, or simply by treating the gasoline with reducing agents, such as sodium hydrogen sulfite, stannous chloride, and acetic acid and zinc. It was concluded that the loss of the antidetonating properties was due to the formation of oxidation products or catalysts, perhaps of the nature of peroxides, acids, aldehydes, ketones, etc., which augmented the detonation. The observation that antioxidation catalysts preserve the detonation characteristics of a cracked gasoline gives further evidence of these oxidation reactions.

Rogers, Bussies, and Ward⁶⁵ found in working with many samples of stored cracked gasoline that there was no appreciable change in the knock rating until at least 15 mg. of gum per 100 cc. of gasoline had formed when determined by the air jet method at 212° F. Beyond this point there was no consistent relation between the amount of gum and the extent of loss of knock rating. They concluded from their experiments that the loss in knock rating was not an important problem, since trouble from gum would arise long before the knock rating of the gasoline was affected.

A further discussion of gum formation is made in Chapter X.

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Chapter IX

Inhibitors of Atmospheric Oxidation of Petroleum Products. Antioxygens

Small quantities of certain reagents prevent the oxidation by air or free oxygen of a variety of substances which undergo oxidation or autoxidation when exposed to air or oxygen at normal temperatures. These inhibitors are termed antioxygens, or sometimes antioxidation catalysts.

In 1822, Moureu and Dufraisse of the College de France, Paris,^{12, 13} published details of their observations in a systematic study of the effect of antioxygens in inhibiting oxidation of such substances as aldehydes, vegetable oils, butter, sodium sulfite, and substances subject to autoxidation, or slow, spontaneous oxidation.

Mardles⁹ gives a good review of the history and theory of antioxygens. Extensive listings of antioxygens are found in the literature.^{7, 10, 12, 15, 16, 18}

Antioxygens have long been used to stabilize against atmospheric oxygen commercial organic compounds which are simpler in composition than petroleum products. Their use in rubber is an example. Although the control of autoxidation in petroleum products is more complex, nevertheless large quantities of inhibitors are now consumed with corresponding economic savings of stock and refining reagents.

The antioxygens first investigated by Moureu and Dufraisse belong to the phenolic type of compounds. Some of the conclusions from their earlier work will make clearer the behavior of these inhibitors. They found, for example, that one molecule of hydroquinone inhibited the slow oxidation by air (autoxidation) of 40,000 molecules of acrylaldehyde, a substance which otherwise is very unstable toward free oxygen; this proportion of catalyst by weight is about 0.0005 per cent. Linseed oil, which ordinarily oxidizes rapidly in air and forms a thin, solid film in a few days, is protected so thoroughly by a small quantity of one of these antioxygens that films of the oil exposed to air for three years still retain their fluidity. Of these phenolic antioxygens, they found that the most active in protecting linseed oil are catechol (ortho-dihydroxybenzene), hydroquinone (para-dihydroxybenzene), and pyrogallol (1,2,3-trihydroxybenzene). Ordinary phenol and resorcin (meta-dihydroxybenzene) are weakly active; the naphthols and guaiacol are more active, whereas phloroglucinol (1,3,5-trihydroxybenzene) may not only fail to retard the oxidation but may

hasten it. However, phloroglucinol under certain conditions is also an anti-oxygen.

Condensation and Polymerization

In addition to the direct degradation of autoxidizable substances, which is proportional to the amount of oxygen absorbed, there is a frequently occurring secondary effect, such as condensation and polymerization, which are induced and catalyzed by an extremely small proportion of absorbed oxygen. Moureu, Dufraisse, and Lotte¹⁷ consider this transformation to be due to the catalytic effect of a trace of peroxides, formed through oxidation, and they cite the conversion of acrolein into the insoluble resin disacryl by a mass of oxygen 0.00001 as great as that of the acrolein converted. In inhibiting such transformations, obviously the antioxidants can play an extremely important role.

Scope of Antioxygens and Autoxidizable Substances

Since their early publications of 1922, Moureu and his collaborators have published over 30 papers on a broad variety of catalysts and on compounds subject to autoxidation. Among the autoxidizable substances examined and found amenable to control are fats; vegetable, animal, and hydrocarbon oils; aldehydes; rubber; etc. Among the most active antioxidants are the tannins; the phenols; and the organic and inorganic compounds of sulfur, of nitrogen, and of iodine. Elemental sulfur is under certain conditions a strong antioxidant, as will be shown later.

Taradoire¹⁹ investigated many of the results of Moureu and Dufraisse and found the phenolic compounds to be the most active inhibitors of the oxidation of aldehydes; but in the protection of linseed oil, he found the aromatic amines to be more efficient than the phenols.

Still later work by Wagner and Brier²⁰ on linseed oil indicates that the aromatic amines are not reactive *per se* but through their decomposition products, and they also find that the amines are more effective than any of the phenols for protecting linseed oil. The relative effectiveness of the four phenols which they investigated is: hydroquinone 100, pyrogallol 70, alpha-naphthol 40, and resorcinol 4. The inhibitors are more effective at ordinary than at elevated temperatures.

Functioning of the Antioxygens

All the antioxidants, when used in small quantities, appear to create an induction period in which the extent of the oxidation is negligible or too small for measurement. At the end of this period, oxidation proceeds rapidly and at about the same rate as an unprotected sample in the same state of oxidation. At the end of the induction period, a comparatively

large amount of the antioxygen is required to check the oxidation even for a short time.

Dupont and Allard⁵ find that less than 0.02 per cent of hydroquinone prevents the autoxidation of pure abietic acid (principal constituent of rosin); but if oxidation has already begun, this quantity only retards it, and 0.1 per cent is necessary to prevent it. A similar disparity is displayed in the proportions of the inhibitor required for the abietic acid when atmospheric oxidation is intensified by an active catalyst, such as 1 per cent of cobalt abietate. Under these conditions, 0.1 per cent of hydroquinone, if added at the beginning, will inhibit the reaction; but if oxidation is first permitted to get under way, about twice as much hydroquinone is necessary to check it.

Regarding the requirement of the larger amount of the antioxygen catalyst to stop oxidation after it has already begun, Moureu and his co-workers¹⁷ point out that the peroxides, which have formed in the absence of the antioxygen and which are oxidizing agents, destroy the antioxygen when it is added later, whereas the peroxides would not have formed in measurable quantity if the antioxygen had been present from the beginning. The antioxygens do not hinder the oxidizing action of strong oxidizing reagents, such as potassium permanganate, hydrogen peroxide, nitric acid, etc., but prevent only free oxygen from combining with the autoxidizable substances. All these antioxygens are themselves oxidizable substances; pyrogallol, an extreme case, when pure is very unstable in oxygen. In fact, Moureu and Dufraisse, after an examination of over 300 substances which possess antioxygenic properties, concluded that the inhibiting action of all antioxygens depends on their own oxidizability.

Postulates as follows have been advanced by Moureu and Dufraisse,¹² which at least permit one to visualize the behavior of the antioxygens: the peroxide of the protected substance, A , is formed, which immediately loses the oxygen to the antioxygen, B , forming $B(O)$, and A is again converted to a peroxide. The two peroxides, $A(O)$ and $B(O)$, are mutually antagonistic and destroy each other with consequent regeneration of the three original components, A , B , and O_2 .

Jorissen,⁸ offering a picture somewhat similar to that of Moureu and Dufraisse, points out that if $B(O)$ acts upon $A(O)$ more readily than it does upon the substance A , it is an antioxygen catalyst; but if it acts more readily upon A than on $A(O)$, it is a pro-oxygen catalyst. The same substance may thus act as a positive or negative catalyst, the behavior depending upon conditions.

A given catalyst may retard the oxidation of one compound and accelerate that of another, and conditions can be varied so that the same substance may be either a pro-oxygen or an antioxygen catalyst. Examples

of both types of the foregoing are shown in the following respective illustrations: methylamine hydrogen iodide ($\text{CH}_3\text{NH}_2\cdot\text{HI}$) acts as an anti-oxygen toward benzaldehyde but as a pro-oxygen toward styrene; ethylxanthamide inhibits the autoxidation of a slightly alkaline solution of sodium sulfite, but accelerates the oxidation of the same sulfite in a slightly acid solution.¹² Many similar examples have been found by investigators.

Almost all investigators¹ now assume that the autoxidation of hydrocarbons is a "chain reaction" in which oxidation of one molecule induces that of another molecule of the hydrocarbon, and that an antioxygen interrupts oxidation by breaking up the succession of the propagated reactions. The antioxygen itself does not possess the property, when thus oxidized, of inducing the oxidation of other molecules. Christiansen in 1924 presented a clear picture of the chain reaction theory. He assumes that, though many collisions take place between atmospheric oxygen and the hydrocarbon molecules, only a few of the collisions result in chemical reaction. "The molecules of the reaction products just after the reaction possess an available energy greatly in excess of the mean energy at the temperature considered. Now these very 'hot' molecules have sufficient energy to activate molecules of the reactants at the first encounter, and when these react, the resultants in their turn again are able to act as activators, and so on. Consequently, it is possible that the occurrence of one elementary reaction will give rise to a whole series of such reactions." The antioxygens take up the surplus energy from the "hot" molecules resulting from these oxidations and prevent further activation of the hydrocarbon molecules.

Selection of Antioxygens for Oils an Empirical Process

For the protection of substances which are fairly uniform in composition, a systematic tabulation of antioxygens can be developed; but in the complex and always variable petroleum products, each arbitrarily defined product must be considered by itself. Certainly different results may be expected when radical changes are made in the source of the crude oil and perhaps even in the conditions of distillation.

As noted elsewhere, a highly refined petroleum product, such as a transformer oil, may in some cases have greater susceptibility to autoxidation than a less highly refined oil or than the unrefined stock. However, the unrefined stock has constituents which are easily attacked by strong oxidizing agents, such as potassium permanganate, ozone, and hydrogen peroxide, over which the antioxygens have no control. Even sulfuric acid oxidizes them, as evidenced by the simultaneous reduction of the acid to sulfur dioxide and water. Some of these oxidizable substances in the unrefined oil are believed to be active catalysts in the autoxidation of the oil (some pro- and some antioxygenic), the net effect on the oil depending on

which type of catalyst is in the ascendency. After thorough refining, the oil is more resistant to the action of strong oxidizing agents than before; but under some conditions it may be less resistant to the slow atmospheric oxidation because of the absence of any antioxygenic catalysts. Moreover, one would expect the refining operations to advance the oil in the direction of simpler homogeneous compounds to such an extent that an individual antioxygen might be found capable of protecting it from atmospheric or molecular oxygen.

Highly Refined Hydrocarbon Oils

Mead and McCabe,¹⁰ of the Massachusetts Institute of Technology, tested 177 substances, all of which they list in their report, for antioxygenic protection of transformer oils. Of these, 48 showed inhibitory properties; outstanding among these 48 were elemental sulfur, nitroresol, and nitrobenzene. These three diminished the gum formation to less than one-fifth that of the unprotected sample under the severe conditions of the test.

Table 89 includes the most interesting oxygenic catalysts examined and all those that decreased the gum formation to 18 to 60 per cent of that of the unprotected sample. The last three substances of the table greatly accelerated sludge formation.

Table 89. Effect of Various Substances on the Deterioration of Transformer Oils.

Substance	Sludge (Based on Sludge Formed in Control Sample) (%)	Substance	Sludge (Based on Sludge Formed in Control Sample) (%)
Control (no catalyst)	100	Turpentine	56
Sulfur	18	<i>n</i> -Octyl alcohol	57
Nitroresol	18	Iodoform	58
Nitrobenzene	19	Bases from crude anthracene	519
Phenylhydrazine	40	Phenyl thiomethane	662
Tolidine (0.03%)	52	<i>m</i> -Phenylene diamine	1240
Cymol	55		

Oils used, Humble and Eagle transformer oils.

Concentration of catalysts, 0.15 per cent.

Temperature of tests, 266° to 284° F.

Time of test, 130 to 168 hours.

The inhibitors diminishing the percentage of gum formation to 60 to 75 per cent of that of the unprotected sample are: pseudo-cumol, menthol, furfural, Hexalin, borneol, Dekalin, iodobenzene, carbazole, pyromucic acid, diphenylhydrazine (0.75 per cent), trioxymethylene, dimethylaniline.

Those diminishing the percentage of gum formation to 75 to 100 per cent of that of the unprotected sample are: *p*-dibromobenzene, diethyl nitrosoamine, pine oil, camphor, hexamethylenetetramine, anethole, pyrogallol, oleic acid, fluorobenzene, dimethylglyoxime, Tetralin, benzene azo- β -

naphthol, oil blue, eucalyptol, acetone extract of crude rubber, glycocoll, phenetole, diphenyl, *p*-iodophenol, α -picoline, furoin, benzaldehyde, amyl-fluoride, piperidine, hydrazine sulfate, oenanthol.

Haslam and Frölich,⁷ also of the Massachusetts Institute of Technology, made a similar investigation on rates of oxidation of highly refined Parke-Davis mineral oil with and without oxygenic catalysts. Dry oxygen was bubbled through different samples of the oil maintained at 266° F. for 1 to 32 hours; 0.01 gram of catalyst per 100 grams of oil was used.

Table 90 shows the antioxygenic activity of some of the compounds. The delay in time required for the development of 0.25 per cent acidity was taken as the basis of measurement, the investigations having justified this procedure. The time for this degree of acidity to develop in the unprotected sample of the oil was two hours.

Table 90. Effect of Catalysts on Oxidation of Parke-Davis Oil at 266° F.

Compound	Delay in Oxidation Caused by Catalyst Hours	Compound	Delay in Oxidation Caused by Catalyst Hours
Phenyl isocyanide	-1 ^a	Diphenylguanidine	1
<i>p</i> -Toluidine	-0.5	β -Naphthylamine	3
1,2,3-Xylidine	-0.5	Ethyl- α -naphthylamine	3
Quinoline	-0.5	Methyl- α -naphthylamine	4.5
Diphenyl	-0.5	α -Naphthylamine	4.5
Aniline	0	<i>p</i> -Aminophenol	5
Tolidine	0	Diphenylamine	5.5
Phenylhydrazine	0	Phenyl- α -naphthylamine	11
Hydroquinone	0	Diphenylhydrazine (un- symmetrical)	18
Oxanilide	0		

^a The minus sign indicates positive catalysis—i.e., oxidation starts earlier than for the pure oil.

When the 0.01 per cent of diphenylhydrazine, $(C_6H_5)_2N \cdot NH_2$, (the most active anticatalyst found by Haslam and Frolich for their special sample of oil) was used, the time required for the protected oil to develop 0.25 per cent acidity was increased tenfold. Whether similar activity would be shown in another oil could be determined only by trial.

In the above investigations of Mead and McCabe and of Haslam and Frolich, the oils, when oxidation set in after a long period of quiescence, were oxidized at about the same rate as the respective unprotected oils.

Mizushima and Yamada¹¹ show that though elemental sulfur may be objectionable under some conditions, it can act as a strong antioxygen in protecting highly refined transformer oils from autoxidation. They dissolved 0.01 per cent of sulfur in a transformer oil, which contained only 0.023 per cent of stable combined sulfur, and exposed it for 100 hours at 248° F. in contact with oxygen at over one atmosphere pressure. They found practically no oxidation of the oil, whereas a corresponding control

sample of the oil without the elemental sulfur was highly oxidized. They also report that sulfur similarly protects paraffin wax, and that isoamyl sulfide, $(C_5H_{11})_2S$, has remarkably strong antioxygenic properties.

Moureu and Dufraisse^{14, 12} show that elemental sulfur can prevent autoxidation; they also give many examples in which compounds of sulfur act as antioxygens.

Light Hydrocarbon Oils

Flood, Hladky, and Edgar⁶ investigated the gum-forming characteristics of unsaturated hydrocarbons, representing types of compounds likely to be found in cracked gasoline. To observe more accurately the changes, they added 10 per cent by volume of the unsaturated hydrocarbon to a straight-run paraffinic gasoline, which alone would not form gum or absorb oxygen under any of the conditions of the experiments. They also made tests with a gum inhibitor, α -naphthol, on these ten per cent solutions. Their abridged data are shown in Table 91.

The fifth from the last column shows the induction period, or the time elapsed before the beginning of measurable oxygen absorption by the olefins. In Experiments 5 to 10, inclusive, the bomb test was discontinued with a given drop in the pressure. The increasing quantities of inhibitor prolong the induction period without affecting the rate of pressure drop or of gum formation after the end of the induction period.

Moureu, Dufraisse, and Chaux¹⁶ use a large variety of antioxygens to inhibit the autoxidation in a petroleum distillate, paraffin wax, decahydronaphthalene ($C_{10}H_{18}$), copra oils, etc.

Butkov⁴ has shown that beta-naphthylamine and aniline check the autoxidation of heptane, or a lighter hydrocarbon than those discussed above.

Baxter² tested several antioxygens in protecting a highly unsaturated gasoline produced from Colorado oil shale and reported that only phenylhydrazine had any appreciable value in preventing either oxidation or gum formation. Unfortunately, he did not discuss the other substances examined.

Brooks³ points out that a very small amount of amines or ammonia may stabilize cracked gasoline in storage against formation of gums and degradation. He finds that the instability is sometimes due to the transformation of neutral sulfuric acid esters into acidic substances, which in turn cause deterioration of the gasoline, but that the gasoline remains stable if the basic substances are present to neutralize the acids. However, in this case the bases are in no sense antioxygens.

As a result of experimentation, it has been shown that the action of atmospheric oxygen is largely responsible for the decrease in the knock rating of a gasoline in storage and for gum formation, especially in the

Table 91. Olefin-Gasoline Mixtures and Gum Inhibitor.

No. Expt.	Inhibitor (%)	Gum by Evaporation of Fresh Material			Oxygen Bomb Test at 212° F. and 100 lb. Pressure			Aging Test (air not excluded)	
		Porc. Dish	Copper Dish	Steam Oven	Time of Heating (Hrs.)	Induction Period (Hrs.)	Pressure (lbs./ sq. in.)	Gum by Steam Oven (mg./100 cc.)	Porc. Dish (mg./100 cc.) 4 mos. 8 mos.
1	Hydrocarbon	159	164	132	4	0.25	65(?)	2444	321
2	2-Methylbutadiene	0	4	>4 ^a	5	162	174
3	2,4-Hexadiene	0	0	2	4	0.25	70	1113	64
4	2,4-Hexadiene	0	0	5	4	>4 ^a	?	3	0
5	2,4-Hexadiene	1.75	0.25	40	595	79
6	2,4-Hexadiene	6	4.5	45	663	9
7	2,4-Hexadiene	8.25	6.75	40	495	..
8	2,4-Hexadiene	10.75	9.25	45	623	..
9	2,4-Hexadiene	11	9.5	40	652	..
10	2,4-Hexadiene	12.6	11.5	45	644	..
11	1,3-Cyclohexadiene	9	43	3	4	0.25	35	1372	242
12	1,3-Cyclohexadiene	1	12	1	4	0.5	35	1822	14
13	1,3-Cyclohexadiene	2	20	1	4	3	35	1655	14
14	Phenylethylene ^b	0	1	11	4	1.5	20	955	17
15	Phenylethylene	0	2	6	4	>4 ^a	10	5	6

^a Over 4 hours.^b Probably contains ethyl-benzene.

cracked gasoline, which contains many chemically active olefinic compounds. In an analogous manner oxygen is known to be the principal factor in the production of the undesirable constituents which develop in transformer and lubricating oils when in use or in storage.

Slow autoxidation is the main cause of gum formation in gasoline and "sludge" formation in insulating and lubricating oils; it may be an important factor in the loss of color in refined products in storage. At present the principal gum inhibitors are the following compounds and their substitution products: mono- and polyhydroxy compounds, aromatic mono- and polyamines, aminophenols, and nitrophenols. The principal color stabilizers are the amines, such as triamyl- and tributylamine.

In Chapter VIII on Antidetonants is discussed the use of small quantities of inhibitors in preventing gum formation and loss of antiknock properties of cracked gasoline, and in Chapters X and XI are given examples of inhibitors against gum and "sludge" formation and loss of color.

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Chapter X

Gums in Cracked Petroleum Products

The problem of preventing gum from forming in gasoline first arose with the production of cracked motor fuels; straight-run distillates are always satisfactorily free from gum. Gums settle out of a chemically unstable gasoline in storage tanks, in pipe lines, and in the motor carburetor, clog the fuel system, and form deposits on the hot parts of the engine, on the stems of the inlet valves, in the intake manifold, etc., and often, but not necessarily, result in loss in the non-detonating properties of the gasoline.

Boeriage¹⁰ believes, however, that the collection of gums on the pistons of an automobile engine is due to abnormal combustion and not to the presence of gum in the fuel. He finds that gum is entirely absent from this part of the engine when the ignition and combustion systems are properly adjusted, but it appears when they are not.

Gruse²⁷ points out that valve stems often become stuck in their guides; but almost invariably this sticking occurs only in the exhaust valve stems, and is due to the lubricating oil on the stems which becomes coked by the exhaust gases and eventually accumulates in sufficient quantity to bind the stems. The gums from the gasoline could not reach these exhaust valves to cause the trouble; and in present operation of cars, the intake valve stems never become stuck with the use of the normal commercial gasolines, although it is possible for them to become stuck if an enormously large quantity of gum is in the gasoline, as demonstrated by Hunn, Fischer, and Blackwood.³²

The chemical nature of gum, as well as the mechanism of its formation, is complex and not thoroughly known. It is accepted, however, that the gum is primarily a product of the autoxidation of the unsaturated hydrocarbons, such as the mono-, di-, and triolefins. The oxidation is doubtless accompanied by condensation and polymerization reactions.

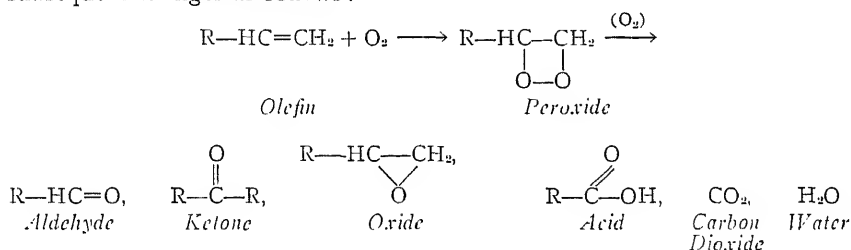
Brooks¹² early published valuable information on the physical properties of gums and the chemistry of their formation in gasolines, especially in cracked products. It is pointed out that the first step in gum formation is the formation of organic peroxides through autoxidation. The peroxides then break up in a complex manner, yielding such products as aldehydes (including formaldehyde), ketones, water, and carbon dioxide; or they may be further oxidized to organic acids. It is shown that diolefins, especially the conjugated dienes, form gums very rapidly, but that the simple olefins may also undergo autoxidation and form gums.

Flood, Hladky, and Edgar³³ find that mono-olefins, unless in high concentration, do not form gums in storage in four months, but that cyclohexene and most of

the olefins attached to a benzene ring, as well as all of the dienes, form gums readily. Schofield⁶⁸ states that gum formation is due to olefins having more than one double bond. Williams and Smith⁷¹ believe the gum-forming constituents are chiefly styrene and indene.

The rate of gum formation increases with the concentration of oxygen, rise in temperature, presence of foreign deleterious substances, and exposure to actinic light. If air and elemental sulfur are entirely excluded from cracked gasoline, it undergoes practically no change when exposed to actinic light. Organic peroxides are to a large extent the intermediate products in the autoxidation processes which yield the gum,^{4, 7, 12, 17, 44, 47} as well as the other degradation products.

Story, Provine, and Bennett,⁶⁵ in a study of gum formation in cracked gasoline, show that the gums result from oxidation processes, a peroxide of the unsaturated hydrocarbon molecule being assumed to form first, which then undergoes change into aldehydes, ketones, acids, etc., as noted by Brooks.¹² They represent the addition of a molecule of oxygen and the subsequent changes as follows:



These investigators studied the action of direct sunlight in accelerating the formation of peroxides in cracked gasoline by pure oxygen and by atmospheric oxygen at normal temperature and pressure. The amounts of peroxides present after different periods of exposure are shown in Table 92 and are expressed in equivalents per 100 cc. of gasoline.

Table 92. Peroxide Formation by Cracked Gasoline.
(Mg. iodine per 100 cc.)

Exposure (hours)	Sunlight with Oxygen (mg.)	Sunlight with Air (mg.)	Sunlight without Oxygen (mg.)	Dark with Oxygen (mg.)
0	0	0	0	0
2	22.0	12.0	4.0	Trace
4	44.0	24.0	4.0	Trace
10	102.0	36.0	4.0	Trace
14	232.0	60.0	8.0	Trace
36	548.0	300.0	8.0	Trace

In these investigations the observation that the gasoline continued to absorb oxygen during periods when the sun was not shining indicated that

periodic exposures to direct sunlight and diffused light promote oxidation. The absorption of oxygen also proceeded in the dark after the end of the induction period, but only slowly at low temperatures. However, during the periods out of sunshine, the quantity of peroxides gradually diminished. The last column is indicative of the slow accumulation of peroxides in gasoline exposed to oxygen in the dark. The next to last column indicates that a little peroxide was formed even though no free oxygen was supplied, doubtless because of oxygen already dissolved in the gasoline.

In other sunlight exposure experiments conducted at the same time, it was shown that the accumulation of gums and organic acids almost paralleled the absorption of oxygen and the formation of peroxides.

Yule and Wilson,⁷⁸ in an investigation of peroxides and gums in gasoline, have shown that peroxides are far more stable in straight-run gasoline than in cracked gasoline. Table 93, from their work, shows the rate of the disappearance of peroxides in straight-run gasoline (oxidized by exposure to oxygen and ultraviolet light) with the rate observed in the same sample after the addition of highly unsaturated cracked gasoline. In this table the peroxides (peroxide number) are expressed as the gram equivalents of oxygen per 1000 liters of gasoline.

Table 93. Effect of Unsaturated Hydrocarbons on Rate of Decomposition of Peroxides.

Time of Heating at 212° F. (days)	Peroxide Number	
	Sample A ^a	Sample B ^b
0	8.0	8.1
1	7.9	5.2
2	6.5	2.6
5	7.0	0.9

^a 35 per cent oxidized straight-run naphtha (boiling range, 300 to 374° F.) and 65 per cent fresh naphtha.

^b 35 per cent oxidized naphtha and 65 per cent fresh cracked gasoline (washed with silver nitrate solution to remove mercaptans).

It appears obvious that the loss of the peroxide oxygen in the "B" experiments is by oxidation of the unsaturated constituents of the cracked gasolines to aldehydes, acids, gums, etc.

Cracked gasolines vary greatly in the rate of gum formation because of differences in their composition, natural gum inhibitors, and conditions of exposure to oxygen. The data of column 2 of Table 94 are typical of the gum formation in cracked gasoline in storage. Without inhibitor the cracked gasoline remains fairly stable for a certain period of time (between two and four months with this sample), after which gum formation proceeds rapidly. The sample protected by the inhibitor remained stable during storage for ten months.

Table 94. Gum Formation in Cracked Gasoline in Storage.

Time Stored (months)	Actual Gum (mg./100 cc.)	
	Without Inhibitor	With Inhibitor (Pyrocatechol)
0	0	0
2	1	0
4	3	1
6	27	1
8	64	2
10	102	4

Table 95 shows the chemical changes in an untreated cracked gasoline ⁶⁸ stored in glass bottles at room temperatures up to 10 months.

Table 95. Storage of Pennsylvania Cracked Gasoline, Untreated.

Month's Storage	0	2	4	6	8	10
Without Inhibitor						
Peroxide No.	0.68	3.20	14.0	35.0	64.0	196
Induction Period (min.)	70	45	35	40	45	55
Gum (mg./100 cc.)						
Copper Dish	113	201	373	719	938	1578
A.S.T.M.	1	6	42	122	138	250
+0.06% UOP Inhibitor No. 1						
Peroxide No.	0.54	0.30	0.27	0.32	0.50	0.55
Induction Period (min.)	345	350	350	315	330	285
Gum (mg./100 cc.)						
Copper Dish	10	4	13	23	22	15
A.S.T.M.	1	1	2	..	3	1
+0.009% UOP Inhibitor No. 4						
Peroxide No.	0.65	0.51	0.65	0.33	0.59	1.23
Induction Period (min.)	330	305	295	255	240	165
Gum (mg./100 cc.)						
Copper Dish	24	13	30	30	31	236
A.S.T.M.	1	3	1	..	2	5

In the uninhibited gasoline the peroxide number rose rapidly; usually when it exceeded 3 units, the A. S. T. M. gum formed rapidly.

It is of interest, but not surprising, that various distillation fractions of gasoline may contain very different percentages of gum or gum-forming

Table 96. Gum Formation in Different Fractions of a Cracked Gasoline During Two Months' Storage at 95° F.

10% Fractions of Gasoline Boiling Point Range (°F.)	Gum by Copper Dish (mg. per 100 cc.)
To 147	4200
147-158	130
158-176	70
176-189	87
189-212	135
212-226	25
226-239	20
239-252	6800
252-275	150
275-302	3650

materials. Mardles and Moss⁴⁴ fractionated a sample of vapor-phase cracked gasoline into ten equal portions, which they stored for two months at 95° F., and then determined the gum content of each by the copper dish method with results shown in Table 96. The experimenters believe that the high percentage of gum in the first, eighth, and tenth fractions is attributable to constituents in these fractions which readily form peroxides, which in turn lead to gum formation.

Cassar¹⁵ made a somewhat similar experiment on a vapor phase-cracked gasoline, but accelerated the gum formation by exposing the freshly distilled fractions separately at 212° F. to oxygen under 100 pounds pressure for four hours and then determined the gum content. The results are shown in Table 97.

Table 97. Gum Formation in Different Fractions of a Cracked Gasoline When Oxidized 4 Hours at 212° F. with Oxygen Under 100 Pounds Pressure.

No. of 10% fraction	1	2	3	4	5	6	7	8	9
Gum (mg. per 100 cc.) (porcelain dish)	240	523	1082	938	785	424	495	436	179

Composition of Gum

Cracked gasoline, unlike straight-run gasoline, has a marked tendency to absorb oxygen and form gums. This property of absorbing oxygen is utilized in some of the tests for determining gum-forming properties, as described later. The chemical analysis of the gum does not throw much light on its constitution. Story, Provine, and Bennett⁶⁵ analyzed the copper dish gum obtained from an untreated cracked gasoline (Column 1 of Table 98) and the gum that settled from cracked gasoline exposed in a glass bowl to sunshine and air (Columns 2 and 3 of Table 98).

Table 98. Analysis of Copper Dish Gum and of Liquid Gum Formed in Gasoline Exposed to Air and Sunshine.

	Copper Dish Gum (100%)	Liquid Gum from Gasoline	
		Original Gum (100%)	Dried Gum (54.4%)
Carbon (%)	70.73	64.97	71.95
Hydrogen (%)	6.95	8.56	7.99
Oxygen (%)	19.51	26.08	19.48
Nitrogen (%)	0.13
Sulfur (%)	0.68	0.22	0.33
Ash (%)	2.00 ^a	0.17	0.25
Hanus iodine value	73	47	95
Molecular weight	200	172	338
Saponification equivalent	191	289	144
Neutralization equivalent	732	625	651
Physical nature	Dark brown, resinous	Dark brown, viscous liquid, sp. gr., 1.0932	Brown, resinous solid 154-160
Melting point (°F.)	208-221		

^a Composed largely of dust.

The copper dish gum (Column 1, Table 98) was examined further; its composition was 13 per cent unsaponifiable matter, 55 per cent water-insoluble organic acids, and 30.5 per cent water-soluble organic acids. The average molecular weight of the water-insoluble acids was 119.

Table 99 contains the analysis of gums produced in a special investigation of Berger and Bost⁷ on the behavior of certain pure hydrocarbons in sunlight and a definite amount of air.

Table 99. Gum Analysis.

Gum	M.P. (°C.)	Molecular Weight	Carbon (%)	Hydrogen (%)	Oxygen (%)	Hydro- carbon Units	Oxygen Atoms
Pinene	85- 90	504	71.92	9.31	18.77	3	6
Limonene	78- 88	693	71.12	8.67	20.21	4	8
Cyclohexene	.. .	304	64.23	9.17	26.60	3	6
Tetralin	.. .	413	74.70	6.70	18.60	3	6
Diallyl	133-142	302

Table 100 contains the chemical analysis of a sample of stored Pennsylvania gasoline and of the gum formed therein and the analysis of the gum from a West Texas stored reformed gasoline.⁴⁸

Table 100. Elementary Analysis of Stored Gasolines.

	Carbon (%)	Hydrogen (%)	Sulfur (%)	Oxygen ^a (%)	Mol. Wt.
Pennsylvania cracked gasoline:					
Entire oxidized gasoline	85.1	13.9	0.06	0.9	
Light distillate	86.1	14.0	0.02	0	
Heavy distillate	86.5	13.5	0.02	0	
Gum residue	69.8	8.7	0.40	21.1	346
West Texas reformed gasoline:					
Gum residue	73.6	9.6	0.40	16.4	294

^a By difference.

Contrary to expectation, gum formation may occasionally be independent of color formation in gasoline. A colorless gasoline may contain a high percentage of gum, whereas a gasoline of a rather dark color may contain none.⁷¹ The nature of the two reactions may, therefore, be different; for this reason the addition of certain substances to gasoline suitable for inhibiting the formation of gum may even be deleterious to the stability of the color.

Actual and Potential Gums

Considerable confusion has existed, and to some extent still exists, in the definition of gums in gasoline; the various methods for their determination give different results, which may also be different from the results obtained in a test with an engine. This confusion comes from the presence in the gasoline, not only of gum as such, but of substances which

are potentially capable of yielding gums on oxidation or through other chemical reactions. As most of the tests for gum content were formerly, and some of them are even now, carried out under conditions favorable to the conversion of the gum-forming constituents to gums, the results are unreliable and in many cases difficult to reproduce. Thus the copper dish test, which was used almost exclusively at first, consists in evaporating gasoline in a copper dish in contact with air. The metal copper is an oxidizing catalyst and often gives an excessively high yield of gums. Therefore, careful standardization is necessary to obtain checks in two determinations, as slight variations in the amount of air present, circulation of air, rate of evaporation, etc., have a variable effect upon the quantity of the potential gum-forming substances converted into gums. The defects of this method have been described in the literature.^{3, 32, 69, 70} Story, Provine, and Bennett⁶⁵ have demonstrated the influence of oxygen in increasing the gum in the copper dish by making the test on cracked gasoline in atmospheres of oxygen, air, steam, and natural gas, as recorded in Table 101.

Table 101. Oxygen and the Copper Dish Gum Test.

Atmosphere Gums (mg./100 cc.) of Gasoline	Oxygen	Air	Steam	Natural Gas
	526	394	34	27

In the determination of gum, especially in research and control work, two different methods are used; one shows the gum actually present which prevents the proper functioning of a motor, and the other the actual gum plus the potential gum content of gasoline, or the total quantity of gum which may be found after comparatively long storage. The actual, or true, gum content is the percentage of material in gasoline which would remain as a residue from the instantaneous evaporation of the gasoline. The copper dish method of evaporation, as discussed above, gives results which are much too high. Since there is no better method of determination, the true gum is frequently estimated as nearly as possible by quick evaporation of gasoline in glass or porcelain dishes on a hot water or steam bath* with or without an air jet playing on the gasoline.^{11, 39, 50} For this true gum a method is desired which would closely check with the amount deposited in an engine. An extremely close correlation cannot be expected, however, for the operation of an engine is not uniform unless arbitrarily controlled for experimental purposes. The percentage of gum deposited in an engine varies within limits with the carburetor adjustment, with temperature, with physical conditions of the gum, etc. For instance, rapid

* The accepted method for actual gums is designated as the A. S. T. M. Method D381-36 (Sept., 1939). In this method 50 cc. of gasoline in a 100-cc. glass beaker is evaporated at 311° F. (155° C.) under an air jet using 1 liter of air per second.

evaporation of gasoline from the carburetor would be conducive to a lower percentage of deposit because of the stronger stream of air carrying the gum into the cylinders, where it is burned.

Induction Period of Gasoline and Storage Stability

A method of accelerating gum formation in motor fuels by heating the fuel and oxygen in a bomb for several hours has been developed. The principal object of the test is to determine the tendency of gasoline to form gum in storage. Zublin⁷⁹ has described in detail the apparatus and the method used by the United States Army and Navy and by the Ethyl Gasoline Corporation.

To make the test, a steel bomb is partly filled with the sample of gasoline, and then oxygen is added under controlled conditions so that the initial pressure is usually 100 pounds at 32° F. The bomb is then heated to 212° F. and maintained at that temperature for the remainder of the operation. A pressure gage indicates whether any oxygen is absorbed by the oil. At the end of the oxidation period the bomb and contents are cooled, and the gum content of the gasoline determined. A drop in the pressure of the oxygen in the bomb in a short time, such as four hours or less from the beginning of the heating, is usually considered to indicate poor stability of the gasoline toward gum formation.

Voorhees and Eisinger⁷⁰ use a glass flask instead of the steel bomb and maintain the oxygen at atmospheric pressure.

During the "induction" period, no apparent absorption of oxygen by the gasoline is indicated by the pressure gage; but at the end of the induction period, or when the gasoline begins to absorb oxygen, the rate of absorption is very rapid. Many investigators assume that the period of induction is due to antioxygenation catalysts in the gasoline, and that when these antioxygens are completely destroyed by oxidation, the gasoline is rapidly oxidized. However, Wagner and Hyman^{71, 75} prefer to interpret the phenomenon as an autocatalytic oxidation process in which oxidation takes place from the beginning, but at too slow a rate for measurement, becoming rapid only when an appreciable quantity of autocatalytic products has accumulated from oxidation of the gasoline.

The oxygen bomb test is used extensively in research and in control work;^{25, 32, 34, 44, 69} but it is not entirely reliable, for some samples of gasoline which are amply stable at normal temperatures readily become oxidized at the higher temperature. Ramsay⁵² and Bridgeman,¹¹ separately investigating the gum acceleration method, predict that the test would be more dependable if induction periods were determined at two or three different temperatures and the data of the gums used to extrapolate the tendency of the gasoline to form gum at its storage temperature.

Recently Yabroff and Walters⁷⁷ have examined experimentally the pressure bomb-induction test in view of the method suggested by Ramsay and by Bridgeman. They used oxygen bombs and assembly identical with the type²³ of the Universal Oil Products Company with slight noted modifications. The data thus far developed (the investigation has not been completed) indicate that a correlation may be established between the time to yield a given gum content in the oxygen bomb, as determined by extrapolation, and storage stability; but the time required to make the test will be excessive except in special cases.

It was observed that the time required for the formation of 10 mg. of gum per 100 cc. of the gasoline (A. S. T. M. Method) was 30 to 75 per cent of the induction period for the various gasolines examined, and that at the end of the induction period the gum content varied from 25 to 100 mg. Of course, the rate of gum formation increased rapidly after the end of the induction period.

It is the opinion of the Research Staff of the Universal Oil Products Company⁶⁸ that neither the induction period nor the copper dish gum test alone is adequate to determine the storage stability of cracked gasoline. A gasoline of long induction period is usually very stable in storage; but if unstable, it usually has a high copper dish gum. A low copper dish gum by itself is also unreliable for determining storage stability, as many unstable gasolines, especially those of low end boiling point, have low copper dish gum. A gasoline having a long induction period and low copper dish gum will be stable in storage; or if a gasoline with a long induction period can be made by means of a gum inhibitor to yield a low copper dish gum, the inhibited gasoline will be stable in storage.

The literature contains many discussions^{25, 32, 34, 44, 69} of the use of accelerated oxidation tests for predicting the stability of gasolines toward gum formation. It may be added here that the oxygen bomb test for gum stability is reliable only so far as it is closely correlated with practical tests made on known types of gasolines. It is known that differences in temperature affect the behavior of the chemical reactions and that the natural inhibitors or added inhibitors in gasolines may also cause great disparity between the behaviors at elevated and at normal temperatures.

Permissible Content of Gum

From experiments in the laboratory and with motors, petroleum technologists have made somewhat tentative deductions regarding the amount of gum in cracked gasolines that is deleterious to an engine. However, it must be understood that these conclusions are not official and probably will be superseded by more definite data.

According to Voorhees and Eisinger^{69, 70} and to Auld,² the maximum

permissible amount of actual gum, which does not indicate the stability of gasoline in storage but is believed to show whether the fuel is satisfactory for immediate use, is about 10 mg. per 100 cc. of gasoline when the determination is made in a glass dish by the steam bath method.

Hunn, Fisher, and Blackwood³² conclude from experiments with a Buick motor and a laboratory apparatus devised to imitate the conditions existing in the intake system of an engine that the actual gum content, when determined under non-oxidizing conditions, can be more than 10 but less than 25 mg. per 100 cc. of gasoline, and tentatively assume that 15 mg. per 100 cc. is permissible. They are of the opinion that when a stability test is made by heating the gasoline to 212° F. in contact with oxygen under 130 pounds pressure, the gasoline is sufficiently stable for storage if the pressure of the oxygen does not drop for 1½ to 2 hours, *i.e.*, if no oxygen is absorbed in that time. This statement is equivalent to saying that if the "induction period" is greater than 1½ to 2 hours under these conditions, the gasoline will remain in storage for any normal length of time without forming a detrimental amount of gum. Sullivan⁶⁶ states more or less arbitrarily that no excessive gum will form in storage for 9 to 10 months if the induction period is 3½ hours or more.

Rogers, Bussies, and Ward⁵³ compared the amount of gum formed in gasoline by aging and that formed by accelerated oxidation at 212° F. with oxygen under normal pressures, and concluded that if the induction period is over 6½ hours, the gasoline in storage will not produce 10 mg. of gum per 100 cc. in a year. They plotted the time in minutes for 10 mg. of gum to be formed in the accelerated oxidation test on new stock against the time in weeks for the same amount of gum to form in actual storage. A straight line expressed the relationship fairly well, although there were some slight discrepancies.

Dean, in a United States Bureau of Mines publication,²⁰ states that motor fuel should not have over 0.03 per cent residue when determined by the copper dish (under oxidizing conditions). This amount is about 23 mg. per 100 cc.

Calingaert¹⁴ says that though the copper dish test gives erratic results, it offers much practical information to the refiner. Thus it is usually found that when fresh samples of gasoline have less than 25 mg. of gum per 100 cc. of oil, they will seldom develop as much as 50 mg. per 100 cc. if kept in storage a few weeks or even a few months; and if the fresh samples have 50 mg. of gum per 100 cc. of oil, they may be expected to develop about 100 mg. in a few months of storage.

According to the American Society for Testing Materials, 15 to 25 mg. of preformed, or actual, gum per 100 cc. of gasoline makes the gasoline unsatisfactory for most automotive engines.²⁶

The Research Staff of the Universal Oil Products Company⁶⁸ states that 7 mg. of gum per 100 cc. of oil (A. S. T. M. Method, glass) is objectionable.

Obviously the quantity of gum permissible in gasoline cannot be expressed with mathematical precision owing to such factors as the somewhat arbitrary conditions of making the gum test, uncertainty of storage time and of temperature, susceptibility of the gasoline to inhibitors, variations in conditions in which the gasoline is used in motors, etc.

CONTROL OF THE GUM CONTENT OF CRACKED PRODUCTS

For many years the principal method of rendering cracked gasolines suitable for motor fuel was limited to the removal of the actual gums, the chemically active constituents which undergo change to form gums, and traces of extraneous material like sulfuric acid^{8, 44, 50} which act catalytically to form gums.

Gums in Acid-Treated and in Acid-Treated and Steam-Distilled Cracked Gasoline

In the different chapters of this book which deal directly with various refining processes, the refining agents which have the property of removing gums and those which increase them have been discussed. Therefore, only a brief summary of the effect of the most important reagents is given here.

The treatment of a cracked gasoline with a small to a normal amount of sulfuric acid, followed by an alkali wash and a water wash, leaves a high percentage of gums; but after steam or vacuum distillation, the fresh distillate is practically free from gum, usually having much less than 5 mg. of gum per 100 cc. of gasoline when determined by the A. S. T. M. Method.

Morrell and Egloff⁴⁶ have determined the influence of temperature and the quantity and concentration of sulfuric acid on the gum content (copper dish) of acid-treated cracked gasoline.

Gums in Acid-Clay Treated Cracked Gasoline

The treatment of cracked gasoline with acid, followed by withdrawal of the sludge and then neutralization with adsorbents, such as fuller's earth or Death Valley clay, leaves in the gasoline a high percentage of actual gum (glass dish), as much as 25 to 100 mg. per 100 cc. However, if the gasoline is subsequently distilled, the distillate is practically free from gums. During the distillation of the neutral oil, an appreciable amount of sulfur dioxide is formed; this results from the decomposition of neutral compounds, represented by such substances as dialkyl sulfates and sulfonic esters. They would account for part of the gum.

Alkalies may sometimes decrease the gum content of cracked oil under certain conditions; for example, when the oil is heated with sodium hydroxide, as described in the chapter on Alkalies. In vapor-phase refining with adsorbents, which is accompanied by a certain degree of rectification, such as in the Gray process, the percentage of gum and of gum-forming substances is lowered. Washing the gasoline with caustic soda solution, or even with water, after redistilling, often helps to lessen the gum and the tendency for its formation, probably because of the removal of products resulting from the decomposition of sulfuric acid esters and other compounds in the oil.^{12, 55} In special instances, however, the gasoline may be made less stable by the caustic washing, possibly because of the extraction of the natural inhibitors.

The process developed by Lachman³⁸ received much consideration for a time. The treatment consists in intimately mixing, in continuous operation, the gasoline in the vapor phase at 300 to 350° F. with a strong aqueous zinc chloride solution. The strength of the zinc chloride solution is kept at 70 to 85 per cent by the proper addition of steam to the gasoline. The oil vapor and solution can be mixed by bubbling the vapor through the solution in a tower containing packing material or by other methods. The vapors can be taken directly from a cracking unit after they have passed through the fractionating tower, or the condensed gasoline can be redistilled and the vapors treated. The boiling point of the strong zinc chloride solution is above the highest temperature of the oil vapors. The time of contact between the oil vapor and salt solution is from 2 to 12 seconds.

The claims for the process are simplicity of operation, high yields of gasoline with low gum content, good color, no loss in the octane rating, and resistance to chemical change in storage.

Table 102 contains data from one of Lachman's reports on treating 5000 barrels of gasoline per day by a redistillation process.

Table 102. Yields in Vapor Phase Refining of Cracked Gasoline with Aqueous Zinc Chloride Solution.

	Barrels	Barrels	Per Cent
Pressure distillate charged	138,135
410° F. end point gasoline	124,550	90.13
Gas oil	13,323	9.64
Loss	312	0.23
410° F. end point content of raw distillate	91.65
410° F. end point gasoline produced	90.13
Plant efficiency	98.35

A comparison of the untreated stock and treated gasoline is shown in Table 103.

Table 103. Effects of Vapor Phase Refining Cracked Gasoline with Aqueous Zinc Chloride Solution.

	Untreated Stock	Treated Gasoline
Gravity (°A.P.I.)	53.2	55.9
Initial boiling point (°F.)	99	90
10% point (°F.)	165	153
50% point (°F.)	297	280
90% point (°F.)	395	377
95% point (°F.)	413	395
End point (°F.)	437	407
Gum (copper dish method) (mg. per 100 cc.)	290	3
Sulfur (%)	0.28	0.19
Mercaptans, as molar	0.017	0.007
Color, Saybolt	...	30

The gasoline is left sour, and subsequent sweetening is required.

A somewhat similar method for refining cracked gasoline has been developed in the cracking division of the Russian Moscow State Oil Research Institute, the GINI Institute.⁵⁶ However, the zinc chloride is used in the solid form rather than in an aqueous solution. A refining tower similar to the Gray process towers is filled with pumice and Raschig rings coated with the zinc chloride. The cracked gasoline vapors are passed through the tower, and from 0.5 to 2.0 per cent of zinc chloride is used per barrel of gasoline. When the zinc chloride becomes exhausted, it is regenerated by washing while still in the tower with benzene, toluene, pyridine, or other solvents, this regeneration being cheaper than dissolving the zinc chloride in water, purifying the solution, and evaporating the water.

Several patents⁵ specify the use of anhydrous zinc chloride for decolorizing petroleum products; but Schulz⁵⁹ states that though zinc chloride has a marked polymerization effect, it otherwise has but little refining action on an oil. A report has been made¹ on the decolorization of cracked gasoline by distilling it at 170 to 340° F. in contact with zinc chloride and washing the distillate with an aqueous solution of caustic soda and with water. A sample thus treated remained colorless for six months and was sufficiently free of gums so that no deposit formed on motor intake valves.

Dunstan²² removes the gum-forming constituents from cracked gasoline by passing the gasoline vapors through pumice, coke, etc., impregnated with an aqueous solution of zinc chloride.

The zinc chloride process stands between the sulfuric acid and the vapor phase-clay treating processes in effectiveness for refining chemically unstable cracked gasoline, like those from the asphalt-base petroleum.

Treatment with Ferric Sulfate

Colin¹⁶ uses a slightly acid solution of ferric sulfate or of a mixture of the ferric sulfate and copper sulfate. In later patents of Cox and McDermott, methods are described for heating the ferric sulfate with the oil, neutralizing, and distilling the oil,¹⁹ and for distilling the oil from a solution of ferric chloride and treating the distillate with alkali.¹⁸

Treatment with Phosphoric Acid

Inasmuch as sulfuric acid, as nearly always used in refining petroleum products, has a marked oxidizing effect on oils, many attempts have been made to use the non-oxidizing phosphoric acid in place of it; but to the knowledge of the writers it has never been used on a large scale. Some of the proposed uses of the acid are, nevertheless, presented below.

According to Melamid and others,⁴⁵ petroleum oils can be deodorized and decolorized by distilling them in contact with phosphoric acid or by passing the oil vapors at 570 to 750° F. through the acid.³⁶ The desired concentration of phosphoric acid is maintained by the addition of water or by the addition of strong phosphoric or pyrophosphoric acid.

Lachman³⁷ has proposed treating crude oils first with sulfuric acid at a little above normal temperature, removing the sludge, and then treating at about 170° F. with phosphoric acid.

Ipatieff and Corson³³ describe experiments on the vapor-phase refining of cracked gasoline with solid phosphoric acid used as catalyst. In the treatment of 5655 barrels of the gasoline per ton of catalyst (with regeneration of the catalyst) the gum was reduced from 56 mg. per 100 cc. to 6 mg., and the color bleached from the original yellow to 27 color Saybolt. Without regenerating the phosphoric acid, one ton bleached 1950 barrels of the gasoline to 29 color. To bleach the gasoline to 27 color with Attapulugus clay, without revivification of the clay, one ton was required for 115 barrels of gasoline. Subsequent to treating the cracked gasoline with sulfuric acid, 0.06 pound of solid phosphoric acid destroyed the alkyl sulfates in the gasoline.

Treatment with Stannic and Stannous Chloride

Anhydrous stannic chloride precipitates asphaltic and resinous substances, as well as certain sulfur compounds, from crude petroleum and its distillates. The reaction is both physical and chemical, and the reagent can be regenerated. Stannic chloride has no action on saturated hydrocarbons, and with various oils the reaction is said to be suitable for the quantitative and qualitative determinations of certain constituents of petroleum.⁶⁷

According to a very old refining process,⁴⁹ about 3 to 6 per cent of

stannic chloride is agitated with the oil, and the oil distilled. In a later process,²⁹ the stannic chloride is distributed upon a carrier, such as fuller's earth, clay, or activated carbon, and the mixture applied to the oil and later separated by filtration.

According to two German patents,⁵¹ stannic chloride is used in the manufacture of insulating oils from coal-tar or shale-tar oils after the insulating oils are first partly purified by extraction with alcohol.

Stannous chloride has been recommended for the decolorization and deodorization of cracked gasoline and for the removal of diolefins and other easily polymerized hydrocarbons. In the proposed method, the gasoline is either heated and refluxed in contact with the stannous chloride, or it is brought as vapor at about 390° F. into contact with the reagent. The treated gasoline is subsequently washed with sodium hydroxide and water and rectified. The stannous chloride can be used repeatedly until its activity decreases, and then it can be regenerated by treatment with hydrogen chloride.⁴³ Because of the expense of this reagent in comparison with other chemicals that accomplish the same purposes, its use under any conditions does not appear to be practicable.

Reduction Reactions

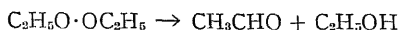
Chemical reagents with reducing properties have not been used extensively in refining petroleum distillates. Chemically active distillates, such as cracked gasoline, when treated with a small amount of a reducing agent in addition to the normal refining processes frequently have less tendency to form gums and are distinctly more stable in color. Experimental data are lacking for an explanation, but it seems fairly logical to assume that these reducing agents remove molecular oxygen which is loosely combined with certain active hydrocarbons, principally unsaturated hydrocarbons, considered by Engler²⁸ as possessing properties of the nature of superoxides, or peroxide, which contain the oxygen as molecularly combined oxygen. Engler examined certain hydrocarbons and found them particularly susceptible to the addition of molecular oxygen. He and his associates have shown that even some of the saturated hydrocarbons are capable of reacting at normal temperatures with oxygen and liberating a small percentage of hydrogen peroxide, and he assumes consequently that this hydrogen peroxide would play an indirect part in the autoxidation of the hydrocarbon.

Treatment with Ferrous Sulfate

McMichael⁴² specifies the use of an aqueous ferrous sulfate solution, under air agitation and preferably made alkaline with caustic soda, for the treatment of petroleum distillates to remove or to prevent the formation of resins and to improve the stability of color. The distillate may

then be moderately treated with sulfuric acid of 70 to 83 per cent concentration and redistilled with steam in contact with a fixed alkali.

Some types of peroxides are decomposed catalytically by ferrous salts, such as ferrous sulfate, without appreciable oxidation of the ferrous salts; but other peroxides oxidize the ferrous to the ferric salt and are, of course, reduced themselves. Willand and Chrometzka⁷³ have investigated the catalytic decomposition of diethyl peroxide by ferrous salts, which proceeds thus:



The diethyl peroxide has less tendency than hydrogen peroxide to oxidize the ferrous salt.

In like manner Yule and Wilson,⁷⁸ in the development of a method for the quantitative estimation of peroxides in gasoline, show that the peroxides in the presence of the ferrous ion are subject to both types of decomposition. It has already been pointed out that washing cracked gasoline with aqueous sulfate solution and then decolorizing it with adsorbents may greatly reduce the amount of gum in the decolorized gasoline, the reduction in gum content doubtless being due to the destruction of peroxides before they can undergo transformation into gums.

Knottenbelt³⁵ has patented a process for the use of ferrous sulfate for the removal of nitric oxide from an oil which has been in contact with nitric acid.

Metal Catalysts in Gum Formation

Certain metals contaminating gasoline have a strong pro-oxidant influence on the gasoline and even on antioxygen inhibitors added to protect it. The common source of the metals, particularly copper, is the containers and conduits used in storage and transportation and the copper salts used in sweetening. Cracked gasoline with as little as one part of copper per million requires 3 to 7.5 times more inhibitor than gasoline without any copper content; the deleterious effect of as little as 0.1 part copper per million of gasoline is measurable.²¹

Table 104. The Effect of Copper Deactivator.

Antioxidant	% by Wt.	Induction Period in Minutes		
		No added copper	1 p.p.m. of Copper	1 p.p.m. copper plus 0.001% deactivator
None		110	30	110
Hardwood tar distillate	0.015	200	50	300
Disalicylethylenediamine	0.001	270	45	430

Downing, Clarkson, and Pedersen²¹ find that disalicylethylenediamine (from condensation of two moles of salicylaldehyde with one mole of ethyl-

enediamine) is an extremely active deactivator of copper, completely destroying its influence when as little as 0.001 per cent by weight of it is added to gasoline containing one part per million (p. p. m.) of copper, as illustrated in Table 104.

It is also pointed out that in storing gasoline containing one part per million of copper and inhibited with 0.0025 per cent of *p*-benzylaminophenol, gum is formed so fast as to make the gasoline unfit for use in six days. Adding 0.001 per cent of the deactivator, or 10 parts per million, kept the gasoline satisfactory as to gum for six months. In contact with metallic copper, a gasoline inhibited with 0.003 per cent of *p*-benzylaminophenol formed prohibitive amounts of gum in five days. The same gasoline containing an inhibitor-deactivator (0.00225 per cent *p*-benzylaminophenol and 0.00075 per cent deactivator) was satisfactory after 55 days. This metal deactivator is not a gum inhibitor and is not itself oxidized by air. It has no undesirable effect on other additives to the gasoline, such as tetraethyl lead or dyes.

Other methods of removing small amounts of metals from gasoline have been proposed. Hopper³¹ washes copper-sweetened gasoline with a little aqueous sodium carbonate solution. For the same purpose aqueous solutions of sodium sulfide^{60, 61} and zinc and ferrous sulfides⁶ have been patented.

Chemical Inhibitors of Gum Formation

The use of gum inhibitors has been extensively investigated. Hoffert³⁰ finds that one volume of cresol in 50,000 volumes of benzene retards the formation of gums in benzene, and a higher concentration of one part in 2500 completely stops it.

Phenol, thymol, and ammonia are discussed as inhibitors by Mardles and Moss.⁴⁴

Bjerregaard⁹ has patented the use of anthracene, phenanthrene, phenol, ortho-, meta-, or para-cresol, and guaiacol, and claims that when these substances are used in quantities of not over 2 pounds per 100 barrels of gasoline, they render the gasoline gum- and cloud-free.

According to Somerville,⁶² aniline, alpha- or beta-naphthylamine, ortho- or para-toluidine, ammonia and acetic acid, aldol, formaldehyde, benzaldehyde, and furfural also have stabilizing effects.

Patents issued to the Standard Oil Development Company and to Fischer²⁴ specify that gum formation in gasoline is retarded by 0.5 per cent, or less, of an alpha-substituted polycyclic aromatic hydrocarbon, such as alpha-naphthylamine, alpha-naphthol, etc.; naphthalene, anthracene, phenanthrene, or other condensed ring hydrocarbons may be substituted for or used with the above compounds. Gum formation is also retarded

by pyrogallol, phenol, hydroquinone, thymol, or other benzene ring compounds with at least one hydroxy group.

As already stated, inhibitors of color change may be different from those of gum formation, and a substance effective in one respect may not help in another. Thus the addition of alpha-naphthol to gasoline is effective in inhibiting the formation of gum, but it may impair the color stability. The condition is not usual, however, unless the inhibitor itself becomes colored. For stabilizing color, the addition of 0.2 to 0.5 per cent of hydroquinone ⁷² or of an aromatic or aliphatic dihydroxy compound, an aromatic amine, a phenol, urea or urea derivative, or an alkaloid, such as brucine or nicotine, is patented.⁶⁴

Egloff, Morrell, Lowry, and Dryer ²³ have made laboratory experiments with 150 compounds for the twofold purpose of finding inhibitors which would stabilize color, gum, and knock rating in certain cracked gasolines, and of correlating the inhibiting action of the chemicals with their chemical structure. Space does not permit a complete discussion of all the data. Table 105, however, shows the behavior of small amounts of trihydroxy-

Table 105. Stability Study of Pennsylvania Cracked Gasoline.

Inhibitor	Untreated	Treated with 3½ lb. of Acid and Redistilled. Effect of Inhibitors				Blend of 30% Untreated Tops and 70% "Bottoms" ^a Treated with 4 lb. Acid and Redistilled. Effect of Inhibitors		
		None	Triresol 0.05%	Hydroquinone 0.01%	Dupont No. 8 0.0125%	None	Hydroquinone 0.01%	Dupont No. 8 0.0125%
Octane No.	73	71	71	71	71	73	71	71
Color, Saybolt	-7	30	28	28	Pink	30	30	Pink
Gum (mg./100 cc.)								
Copper dish	217	33	15	59	14	103	94	4
Air jet	8	8	8	0	10	2	0	0
Induction period in oxygen bomb (min.)	75	60	180	225	over 240	45	225	225
Storage tests:								
One month:								
Octane No.	69	58	67	69	66	55	71	72
Color, Saybolt	2	28	27	27	Red	30	30	Red
Gum, Copper dish	350	229	28	44	11	500	57	7
Air jet	20	98	4	2	6	104	0	4
Two months:								
Octane No.	69	49	67	68	66	43	69	70
Color, Saybolt	1	30+	29	29	Red	30+	30+	Red
Gum, Copper dish	320	470	42	31	8	968	65	8
Air jet	44	226	18	6	6	216	2	2
Three months:								
Octane No.	69	47	67	69	67	34	68	70
Color, Saybolt	1	30	25	30	Red	26	30	Brown
Gum, Copper dish	485	565	63	139	16	1120	121	17
Air jet	38	244	10	10	2	674	6	2

^a The "bottoms" pertain to the gasoline left after the first 30% fraction is distilled.

toluene, hydroquinone, and Dupont No. 8 (inhibitor), particularly in preventing gum formation and loss in knock rating and in prolonging resistance to oxidation in the oxygen bomb test. The table shows that the samples of gasoline kept in storage for three months without inhibiting agents formed from 24 to 335 times as much gum as the protected samples, as determined by the air jet method.

Rogers and Voorhees⁵⁴ report an extensive investigation on the control of gum formation in cracked gasoline by means of many antioxygens. Table 106 shows the most active of the inhibitors. These are aminophenols and derivatives of the aminophenols in which one hydrogen atom of the amine group has been replaced by a radical. These substitution compounds are much more active than the parent aminophenols and have other interesting characteristics. For example, 0.2 per cent of benzylaminophenol dissolves in gasoline, and only 0.01 per cent of methylaminophenol dissolves. The former is not soluble in water, whereas the latter is water-soluble and consequently is extracted if water comes into contact with the gasoline. The benzylaminophenol does not injure the color of the gasoline, but the methylaminophenol does injure it. If both hydrogen atoms of the amino group are replaced with radicals, the antioxygen activity of the molecule is lowered considerably.

Table 106. Aminophenols as Antioxygens.

Antioxygen	Concen. (Per Cent)	Induction Period (minutes)	
		With Antioxygen	Without Antioxygen
<i>p</i> -aminophenol	0.005	270	55
<i>o</i> -aminophenol	0.005	280	55
4-amino betanaphthol	0.002	205	135
2-4 diaminophenol	0.0005	130	90
<i>p</i> -methylaminophenol	0.002	495	95
<i>p</i> -methylaminophenol	0.001	305	90
<i>p</i> -methylaminophenol	0.01	1800	55
<i>p</i> -benzylaminophenol	0.005	665	120
<i>p</i> -benzylaminophenol	0.002	340	120
<i>p</i> -phenylaminophenol	0.005	550	120
Benzal- <i>p</i> -aminophenol	0.002	120	80
Cinnamal- <i>p</i> -aminophenol	0.002	100	80

In Table 107 Rogers and Voorhees⁵⁴ compare the antioxygen power of *p*-benzylaminophenol with that of other phenolic compounds.

Table 107. Inhibitor Effect of Substituted Phenolic Compounds.

Antioxygen	Induction Period for 0.002% Concentration
Control	130
Hydroquinone (<i>p</i> -dihydroxybenzene)	140
Catechol (<i>o</i> -dihydroxybenzene)	150
α -Naphthol	190
Pyrogallol (1,2,3-trihydroxybenzene)	310
<i>p</i> -Benzylaminophenol	345

Because of their general practicability, the principal gum inhibitors for motor fuels consist of alpha-naphthol, monobenzyl-para-aminophenol (BAP of the trade), a wood-tar distillate^{40, 76} containing mixtures of such products as cresol, catechol, ethyl guaiacol, mono-ethers of pyrogallol, xlenols, etc. The principal stabilizers of color of motor fuels are tributylamine and triamylamine, described by Sorg.⁶³

Lowry, Egloff, Morrell, and Dryer⁴¹ have reported on the use of gasoline dyes which also have gum-inhibiting properties. Typical examples are shown in Table 108.

Table 108. Gum Inhibitor-Dyes.

	Color Index No.	Solvent	Cyclohexene No. (min.)	Color in Gasoline
Azo Dyes:				
Oil Brown	73	Benzene	110	Red
Orange base	20	Hexone	220	Yellow
Azine dyes:				
Induline base B	860	Benzene	550	Pink
Nigrosine base N	864	Hexone	160	Red-violet
Triphenylmethane dye,				
Victoria Blue B base	729	Hexone	125	Brown-red
(Diphenylamine)	...	Hexone	80

As these inhibitors are oxidized and, like all inhibitors, lose their power to prevent gum formation, they also fade; the loss of color may thus give an indication of the time at which the gasoline is no longer protected.

Byers¹³ has reviewed the patent literature on gum inhibitors and gives a list of 125 United States patents.

The gum inhibitors permit the production of stable gasoline much more economically than formerly when the stability depended on drastic refining methods alone. Unless an excessive amount of combined sulfur must be removed, gasoline is now usually refined to the necessary specifications, and then the qualities stabilized by a very small quantity of the inhibitor. This procedure results in a saving in the refining agents and in the motor fuel formerly destroyed in the refining. The economy in using inhibitors is described in the literature.^{57, 76}

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Chapter XI

Deterioration of Lubricating and Similar Oils. Addition Agents

The term "lubricating oil" includes many products used to lubricate different types of machinery. Sometimes it is broadened to include such oils as transformer and insulating oils, which have little, if anything, to do with lubrication. Lubricating oils are generally considered not to include greases, which are solid, or semisolid mixtures of soap and mineral oils. The dividing line between lubricating oils and greases is not definite, however, because mineral oils may contain certain quantities of soaps and still remain liquid at ordinary temperatures. The term "liquid greases" is occasionally used to designate such products.

Various kinds of machinery require different types of lubricating oils; for this reason, the actual number of lubricating products manufactured in the petroleum industry is large. These products may vary in viscosity, in the source of the crude oil from which they originate, in the extent they are influenced by addition agents, etc. Complete description of the products is beyond the scope of this book; the discussion is limited primarily to the usual motor oils, although aviation, transformer, turbine, and other types of oils are considered briefly.

Oxidation Sludges

When used in an automobile engine, a lubricating oil not only becomes contaminated with the higher-boiling constituents of gasoline and coke-like products from the combustion chambers, dust from the roads, and worn fragments from the bearings, but some of the oil itself slowly undergoes partial oxidation from contact with the air and eventually forms deleterious products in sufficient quantity to render further use of the oil unsafe. The oxidation forms organic acids, which attack the metal parts of the motor and produce metal soaps insoluble in the oil, and other products which undergo transformation by polymerization, condensation, etc., into semisolid, gum-like material, for the most part insoluble in the oil. The material separating from the oil is known as lubricating oil "sludge," a term in no way synonymous with the acid or alkali sludge resulting from refining operations.

The apparent viscosity of an oil which has long been used in an automobile may be greater or less than that of the original oil, the condition

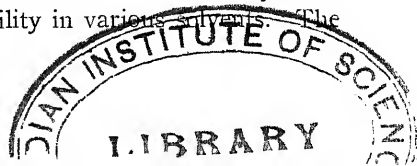
depending upon the relative proportions of sludge dispersed in the oil and the amount of gasoline dissolved in it. If the automobile engine is run at a relatively warm temperature so as to produce a large percentage of sludge and to evaporate the gasoline and lower boiling oil fractions, the viscosity becomes greater than that of the new oil; but if the engine is operated at a low temperature so that less sludge forms and gasoline collecting in the oil does not evaporate, the net effect is a decrease in the viscosity. The sludge obviously interferes with proper lubrication by preventing free access of oil to the bearings and increasing the internal friction of the oil; and it may entirely stop the flow of oil in the circulating system.

Oils used for such purposes as lubricating high-speed spindles of knitting machinery, or bearings of high-speed steam turbines, or for insulating electrical switches and transformers are not subject to the diluting action of gasoline and usually not to contamination with dust, but they are subject to acid and sludge formation through oxidation. Any appreciable deterioration in these oils makes them unfit for use. In high-speed bearings the sludge prevents proper lubrication, and any increase in the viscosity increases the power consumption. In transformer oils the sludge interferes with the high electrical insulation quality and with the free circulation of the oil which carries away the heat from the electric windings and cores. The difficulty in cooling is further augmented by the deposition of sediment on the surfaces of the electrical equipment, forming a barrier against heat transfer. Transformer oils lose their resistance to emulsifying with water as soon as they undergo even a little oxidation; and if then exposed to water, as is often unavoidable, they become emulsified and soon lose their dielectric properties.

Oils which contain dissolved oxygen or are exposed to oxygen in storage gradually form sludge. The sludges are not identical in different oils nor in the same oil when subjected to different kinds and degrees of refinement or conditions of service.

Chernozhukov¹² has made a rough classification of the sludges produced from the heavier petroleum products; namely, (1) sludges which are formed by polymerization and oxidation of tarry substances (non-existent in refined oils); (2) distinctly acid sludges which are formed by the oxidation, condensation, and polymerization of the more chemically reactive hydrocarbons in the refined oil (these sludges are viscous and are brownish in color); and (3) sludges which consist of iron or copper salts of organic acids (these sludges are formed in service by oxidation of the oil and subsequent reaction with metals).

The non-acidic constituents of sludges are classified in an arbitrary manner, as are the asphalts; that is, on the solubility in various solvents. The



constituents of the sludge soluble in petroleum ether and not adsorbed from the petroleum ether by flordin or similar adsorbents are classified as oils; the constituents soluble in petroleum ether but removed from the petroleum ether by adsorbents are resins; the constituents insoluble in petroleum ether but soluble in benzene are asphaltenes; the constituents insoluble in benzene but soluble in carbon disulfide are carbenes; and the constituents insoluble in all of these solvents are carboids. All these constituents contain hydrogen and carbon and practically always oxygen and sulfur. The ratio of their content of hydrogen to carbon decreases in the order in which they are enumerated, or with the decrease in their solubility characteristics. They have a tendency to undergo chemical change under the action of light or oxygen and possibly to some extent on mere standing in the absence of light or additional air. These chemical changes produce a gradual transformation of the sludge into the less soluble products.

Kalichevsky and Fulton³⁴ review the various methods of analyzing asphaltic substances by extraction with solvents and note in particular Marcusson's³⁰ method, which is now in more or less general use.

Chemical Composition of Lubricating Sludges

The chemical analysis of lubricating sludges is extremely difficult, and much work is yet necessary before the chemistry of the products and of their formation can be made clear. A deposit of sludge formed in the water-cooling compartment of a Ridgeway turbine, analyzed by Blakely,³ contained 0.5 per cent moisture, 43.3 per cent oil which was soluble in petroleum ether, 50.4 per cent material insoluble in petroleum ether but soluble in ethyl ether, 2.2 per cent asphaltic material insoluble in the above reagents but soluble in chloroform, and 4.4 per cent material insoluble in all the foregoing reagents and consisting chiefly of metallic iron. Salathe⁴⁸ analyzed a sludge from the lubricating oil used in a 25,000-kw. turbine; it contained 42.5 per cent water and 13.6 per cent acids of aliphatic and naphthenic types, as well as traces of acetaldehyde, soaps, and esters. Stadnikov and Vozzhinskaya⁴⁹ found that a brown deposit, which they separated from a used transformer oil by filtration, lost 0.70 per cent in weight on being heated at 212° F. in an atmosphere of hydrogen and contained 13.16 per cent of ash, in which iron, copper, lead, and tin were identified. On destructive distillation, the sludge yielded 5.0 per cent water, 49.0 per cent oil, and a small amount of tar and carbon dioxide. The presence of sulfoacids was proved. Boisselet and Mouratoff⁴ report that a deposit from a transformer oil consisted exclusively of salts of organic acids and contained 5.8 per cent iron, 2.35 per cent lead, and 0.14 per cent aluminum. According to Chernozhukov,¹² a sludge from a turbine oil contained 35.5 per cent water, 29.5 per cent oil, and 35.0 per cent materials insoluble in gasoline (16.5 per cent

of the material insoluble in gasoline was soluble in alcohol, and 72.6 per cent was soluble in benzene; the alcoholic solution contained organic acids and organic salts of iron, and the benzene solution contained asphalt and organic salts of iron and copper; the part insoluble in benzene and alcohol contained 13.92 per cent iron and 5.06 per cent copper; the rest was silica (dust), carbon, etc.).

Formation of Sludges

It is generally accepted that the chemical changes in lubricating oils are due to atmospheric oxygen and that these changes are affected by the nature of the materials with which the oil comes in contact. It is, therefore, highly desirable that the oils in service be protected whenever possible from oxygen and air. Under oxidizing conditions, an oil forms alcohol-, aldehyde-, and ketone-like substances, some of which are further oxidized to acids (asphaltic acids), probably of the hydroxy-carboxylic type. These acids attack the exposed metals and form metallic soaps. In addition, condensations occur, initiated by the first oxidation products, probably the peroxides, and yield sludges which are insoluble in the oil and which may or may not absorb still more oxygen, the tendency to absorb more oxygen depending on the composition and the physical conditions of the sludges. All these chemical reactions are greatly accelerated by heat; and because of different reaction rates for different hydrocarbons at higher and lower temperatures, the eventual sludge formed at a higher temperature may not be similar to that formed at a lower temperature. For more detailed description of these changes, the reader is referred to the original literature.

As implied above, the "aging" of lubricating oils occurs only in the presence of oxygen, even traces of which are sufficient to promote undesirable but extensive reactions. According to Yamada,⁵⁸ transformer oils, which form sludge readily when heated with air, do not do so in the inert atmosphere of carbon dioxide, nitrogen, or hydrogen, or in a vacuum, although traces of oxygen, such as may be present in an inert gas, may be sufficient to produce the sludge. On the other hand, Incze³¹ and von der Heyden and Typke²⁵ have reported that light in the absence of air may have a decided effect on oils which are unchanged in the dark, and that tar may develop in transformer oils standing in the dark, both in partially filled and in completely filled containers. These last observations are, however, subject to question since it is difficult, if not impossible, to free the samples from air completely, and there is always the possibility that traces of air have been left in the oil. Moureu and Dufraisse, whose work was discussed in Chapter IX, have shown that a very minute quantity of oxygen may act catalytically to bring about extensive condensations.

Investigators^{19, 44, 47} claim that in highly refined oils the acids which

form are stable and do not produce sludge readily, whereas in the unrefined oils these acids are unstable and immediately change into sludge. Marcusson and Bauerschäfer³⁸ conclude from their experiments that sludges, on standing or on heating or on further oxidation, are gradually transformed into more insoluble asphaltenes, which settle out of the oil. On the other hand, sludge is known to be formed at times by oxidation reactions in which organic acids are not involved,⁴¹ and, therefore, the acid number cannot be accepted as a true criterion of the oxidizability of oils or of the degree of oxidation.⁵¹ Sludge and acid formation must be considered as somewhat independent of each other and not as running parallel in different oils or under different conditions in the same oil. This observation, however, does not preclude the possibility that some of the acidic substances formed may undergo polymerization and condensation reactions, and thus contribute to additional quantities of precipitated sludge.

In samples of oil withdrawn periodically in laboratory oxidation tests or engine tests, it is often observed that the acidity of the oil increases stepwise rather than continuously. Further studies reveal that the formation of sludge is greater during the periods when the acidity of the oil appears to remain about constant rather than when it is increasing. This behavior indicates that at least part of the sludge formation comes from the acidic substances formed during the first stages of oxidation reactions. According to Stadnikov and Vozzhinskaya,⁶⁰ the formation of sludge is frequently accompanied by a decrease in the acidity of the oil because of the condensation of acids into sludge, Baum² shows that the tar number obtained in heating the oil with oxygen is no criterion of the stability of the oil in use. According to von der Heyden and Typke,⁵⁰ the acid value of oxidized oils and their tar numbers, as obtained above, bear no simple relationship because of the variations in the molecular weight of the acids formed; a high acid number and a low tar number may indicate acids of high molecular weight. Stäger⁵⁸ reports that two oils with identical "tar numbers"⁵⁵ may yield different amounts of sludge when heated in air.

Although the conditions of preparing oils and their origin have a great influence on their stability, Rodman and Maude⁴⁵ point out that satisfactory transformer oils are made from either asphalt- or paraffin-base crude oils. It is of interest that German specifications for transformer oils require lightly treated products, but British specifications generally require oils treated with very large quantities of sulfuric acid. Both types of oils apparently give satisfactory service in these respective countries, a condition which may be partially explained by the differences in the design of the transformers in the two countries.

Typke⁵⁶ gives a very good survey of the available information on the action of oxygen, temperature, time, light, electric field, etc., on the deterioration of mineral oils.

Oxidation Tests

The quality of lubricating, transformer, and turbine oils that enables these oils to resist deterioration in use cannot be determined by physical

tests alone, and as yet no one chemical method is entirely satisfactory. The accelerated oxidation methods of the laboratory do not necessarily duplicate service conditions, and the actual testing of the oils under normal operating conditions requires too much time. However, many published observations have added to the knowledge of this complex problem; some of the more important conclusions are considered in this work.

Large petroleum companies evaluate their oils by extensive engine tests under varied conditions both in the laboratory and on the road. This procedure is necessary because tests under one set of conditions may give results very different from those under another set of conditions; and to be marketable, an oil must be stable under all the conditions that may be met in service.

Certain of the unsaturated hydrocarbons produced by overheating the lubricant stock during distillation, and otherwise, are subject to oxidation reactions; because of this effect of the olefins, the solubility of the oil in sulfuric acid has been tested as a measure of the oxidizability of the oil, but no correlation exists.¹⁰ Likewise, no correlation exists between the resistance of oils to oxidation and their iodine number,²⁷ bromine number, or formolite number,⁴³ although Musatti and Pichetto report a relationship between the resistance of oxidation and the amount of the oil dissolving in liquid sulfur dioxide which is a good solvent for aromatics and unsaturates. However, in the opinion of the writers, such a correlation seems to be accidental rather than general.

Tests were devised for determining the oxidizability of oils by measuring the rate of oxygen absorption. Evers and Schmidt¹⁷ try to show that the aging curve of an oil may be expressed by an equation:

$$y = 2.3 C \log x + K$$

in which y and x are the amount of oxygen absorbed by the oil and the time, and C and K are constants, varying with the temperature, composition, physical character, and proportion of catalyst used in their procedure. They claim that from the aging constant thus obtained, the saponification value, acid value, and tendency to polymerize during various stages in aging can be calculated rather closely. However, it is very doubtful whether the results of such tests can be correlated with actual service conditions, which involve a large variety of factors other than those considered in the foregoing test.

Two general types of laboratory tests are now in use for determining the oxidizability of mineral oils. In one type the oil is exposed under controlled experimental conditions until it begins to break down; in the second type, which is more popular because of greater simplicity, the oil is oxidized for a definite length of time, and then the changes in some of its properties are measured—usually the increased acidity, the amount of sludge, and the

color. The tests consist in bubbling air or oxygen through the oil or in exposing the oil to air or oxygen for a definite length of time at elevated temperatures, with or without catalysts, such as copper.

All the laboratory test data have the common defect that they cannot be made to correlate sufficiently closely with the results obtained in service; the reactions which take place in the oil under accelerated conditions are not identical with those in normal use. For this reason the tests made over longer periods of time under less severe conditions are, as a rule, much more reliable than those made in a short time under severe test conditions. In general, laboratory tests must be regarded as indicating only relative and not absolute stabilities; even then the comparison should be made on oils from very similar sources.

Tests involving metal catalysts in the oil are very susceptible to "poisoning" effects, as a poor oil may form a coating on the surface of the metal and render it inactive. On the other hand, tests in which metals are not used are not entirely reliable, as a trace of dust or impurity unwittingly introduced into the oil may act as an accelerator and give unduly high results. In using metal catalysts, great care must be taken to maintain a constant ratio of the oil volume to the metal surface and to insure that the surface of the metals is properly prepared. Otherwise even the laboratory results cannot be duplicated.

Most of the laboratory tests are made in the presence of metals, the catalytic action of which is always distinctly pronounced. Such a procedure has been preferred by many investigators because of the fact that the oils are in constant contact with different metals when in use. Copper alone or in combination with other metals is very effective in catalyzing oxidation and sludge formation in oils.^{24, 36} Yamada⁵⁷ finds that lead, zinc, iron, and magnesium tend to reduce the acidity of transformer oils when the oils are heated for 100 hours at 284° F. in contact with the metals. This reduction is at least partially explained by the formation of metallic soaps. Copper, brass, silver, and lead increase the quantity of sludge when less highly refined oils are exposed to air, whereas magnesium, tin, aluminum, and zinc lessen it. Yamada also concludes that metals which tend to accelerate the formation of sludge usually accelerate the formation of acid.

Stäger⁵² reports that the formation of sludge in transformer oils is increased by copper, brass, rheotan, constantan, tin, and zinc, but that sludge formation is not affected by nickel, iron, and aluminum. Lead, zinc, and copper are attacked by the organic acids formed in the oil.

Certainly the metals affect the rates of certain types of reactions; and at higher temperatures, such as those of the proposed laboratory tests, different types of degradation products are expected in oils in contact with metals from the products obtained in the absence of metals. It cannot be con-

cluded, however, that the results obtained by the use of metals in the oxidation tests give true indications of the performance of the oil in actual service.

As mentioned before, a large number of oxidation tests has been devised for oils. A few of the most common tests are presented in Table 109 for illustrative purposes.³³

Table 109. Summary of Some of the Common Lubricating Oil Oxidation Tests.

	Temperature (°C.) (°F.)		Time (hours)	Atmos- phere	Catalyst	Quantity of Oil
Anderson	100	212	100	Oxygen	Cu + Fe	60 g.
Belgian	170	338	5	Air	None	40 cc.
British Air Ministry	200	392	24	Air	None	40 cc.
Brown-Boveri Trans- former	112	234	72/168	Air	Cu	1000 cc.
Brown-Boveri Turbine	110	230	72	Air	Cu	200 cc.
French	150	302	5/50/125	Air	None	10 g.
German Tar (Kissling)	120	248	70	Oxygen	None	150 g.
Indiana	172	342	x "	Air	None	300 cc.
Italian	110	230	300	Air	Cu	40 g.
Life (Snyder)	120	248	To sludge	Air	Cu	1000 cc.
Michie	150	302	45	Air	Cu	100 g.
Sligh	200	392	2½	Oxygen	None	10 g.
Socony	177	351	168	Air	Fe	300 g.
Swedish	120	248	70	Oxygen	None	150 cc.
Swiss	115	239	168	Air	Cu	1000 cc.
U.S.S.R.	120	248	70	Air	Cu	100 cc.

^a Time required to form 10 mg. or 100 mg. of sludge.

Refined Oils and Oxidation

Opinions differ as to the relative susceptibility to oxidation of lightly refined and heavily refined oils, or the influence of the refining on the oxidizability of the oil. Gurwitsch²¹ states that unrefined oils and distillates are oxidized much more readily than refined products because of the more complex compounds and asphaltic substances in the original oil. This statement certainly would apply to cracked distillates, particularly those from vapor-phase cracking; it also applies to mediumly refined kerosene and lubricating oils in comparison with the unrefined stocks.

Von der Heyden and Typke²⁹ find that highly refined transformer oils have a greater tendency to form sludge from oxidation than the less refined oils. The highly refined water-white, or medicinal, oils are known to be unsuitable for use as transformer oils.³⁷

Butkov⁹ reports that oils heavily treated with fuming sulfuric acid oxidize in use more rapidly than a less refined oil. Many other investigators hold the same opinion.⁴⁰

For this unusual behavior of the especially highly refined oils, an explanation is offered in the assumed destruction of protective agents, or anti-oxygens, in the refining process. Von der Heyden and Typke²⁸ report that

on mixing a superrefined transformer oil with a less highly refined oil, the blended oil is more resistant to oxidation than the superrefined oil. Butkov,⁵ in a similar experiment, finds that the addition of 25 per cent of unrefined oil to a refined insulating oil increases the resistance of the insulating oil to oxidation.

From the reports of investigators in various parts of the world, it appears certain that the degree of refining has different effects on the oils in their resistance to oxidation by the air. Flamang¹⁸ reports his investigations on the effect of the amount of acid on the resistance of transformer oils to autoxidation when in actual use and when tested in an artificial aging process. With amounts of acid ranging from 3 to 30 per cent of the oil, he had found at the time of making the report that the stability of the oils toward oxidation increased with the amount of acid used.

Somewhat similar to the data of Flamang are the many reports on the resistance to oxidation of various reclaimed lubricating oils, which have been given additional refining after use. Reclaimed oils are usually less readily oxidized than new oils²² in an artificial aging test, such as the Sligh oxidation test. However, in these reclaimed oils, the total degree of refining has not been carried nearly so far as that of the transformer oils.

The work of Ford and others^{19, 44, 47} shows that a highly refined oil, such as a transformer oil, under oxidation conditions tends to produce fairly stable organic acids, which do not readily change into sludge, and that the simultaneous production of sludge in the oil through other reactions is small; whereas the acids developed in an unrefined oil are unstable and automatically change readily into sludge. No corresponding data for new and reclaimed lubricating oils, such as those used in automobiles, have been published. It would be of interest to know the relationship of the proportions of acid and sludge produced in these oils, since much of the oil is reclaimed and re-used. These oils, as mentioned above, lie in degree of refinement between the unrefined stock and the highly refined oils.

Apparently the cause of these somewhat contradictory statements may be generalized as follows. Crude oils contain many substances, some of which may act as accelerators and others as inhibitors of oxidation. In refining, both kinds of substances may be subject to removal, but perhaps to different degrees. The relative proportion of accelerators and inhibitors left in the refined oil may determine to a large extent its relative stability to oxidation. It is well known, for instance, that a wash with sodium hydroxide may either stabilize an oil or render it more susceptible to oxidation. If the acidic or phenolic substances in an oil are predominantly accelerators, the caustic wash will stabilize the oil; but if they are inhibitors, the wash will render it less stable. A generalization that all phenolic substances act as inhibitors is incorrect. The inhibitors and accelerators of oxidation

can be removed from the oil by sulfuric acid or other refining agents as well as by washing with caustic soda solution.

It is possible to visualize an oil refined to such an extent that the finished product is made up principally of highly stable compounds. Such an oil would be stable and not need inhibitors for its further protection. Two oils may thus be equally stable, one containing less stable hydrocarbons protected by inhibitors, and another containing highly stable hydrocarbons and not protected by inhibitors.

Deterioration of Lubricating Oils in Engines

The previous discussion of the deterioration of lubricating oils pertains primarily to the chemical nature of sludges rather than to their practical manifestations. However, the sludges or engine deposits are classified differently by the operator of the engine. Four major groups of sludges are recognized: those that interfere with the distribution of oil in the engine; those that cause a gradual lowering of engine efficiency, requiring overhauling of the motor; those that interfere with the proper functioning of some engine parts and result in interrupted service without causing actual damage to the motor; and those that do not interfere with engine operation but contribute to the difficulty of overhauling the motor. These sludges are discussed in detail by Stewart and Story.³⁴

The first type of deposit is represented by the lacquers and sludges (so-called "coffee grounds"), which may plug the oil passages, interfere with free lubrication, and cause failure or scoring of the cylinders.

The second type of deposit is lacquers, carbon, or a combination of both, which form on the pistons and interfere with the ring action, and thus result in high oil consumption and in passage of gasoline into the oil sump.

The third type of deposit is usually composed of lacquers formed on various parts of the valve mechanism, which interfere with the valve action. Such deposits may also interfere with the operation of the fuel pump.

The fourth type of deposit may be found in the timing gear chamber, on the crankshaft, crankcase walls, cover plates, in valve chambers, etc. The analysis of engine deposits in Table 110 has been given by Stewart and Story as representative of the deterioration products from the lubricating oils.

It is observed that the sludge may form a deposit on the various parts of the engine or that it may remain suspended in the oil in a colloidal state of dispersion. Deposits may resemble lacquer surfaces, "coffee grounds," mud, or carbon of a fluffy or hard consistency. These deposits may contain variable quantities of metals, worn from the different parts of the engine, and dust from the road. The "wear" may take place even in the absence of serious sludge deposits if the acidity of the oil rises through

Table 110. Analyses of Engine Deposits.

	Naphtha Soluble (Oil) ^a % of Sample	% Weight of the Actual Sludge Deposit				Composition of Ash (% by Weight)	
		CHCl ₃ Soluble	Insoluble in CHCl ₃	Sulfated Ash	Carbon, etc.	Lead Sulfate	Iron Oxide, etc.
1. Oil pan "coffee grounds"	45.1	9.3	90.7	14.4	76.3	51	49
2. Oil pan "coffee grounds"	6.5	5.3	94.7	13.5	81.2	95	5
3. Sludge, single-cylinder laboratory test engine	72.0	53.0	47.0	4.6	42.4	95	5
4. Synthetic "coffee grounds"	60.4	11.3	88.7	7.5	81.2	95	5
5. Under piston crown deposit	11.5	7.8	92.2	60.0	32.2	95	5
6. Winter valve chamber deposit	69.0	6.9	93.1	16.2	76.9	95	5
7. Oil pan sludge	35.4	24.0	76.0	56.2	19.6	95	5
8. Oil pan sludge	...	13.3	86.7	62.0	24.7	95	5
9. Crankshaft deposit	63.8	42.0	58.0	26.4	31.6	95	5
10. Valve cover deposit	58.1	34.0	66.0	17.6	48.4	95	5
11. Breather pipe deposit	48.8	54.0	46.0	21.8	24.2	95	5
12. Piston head deposit	1.9	0.6	99.4	67.2	32.2	95	5
13. Combustion chamber deposit	1.2	0.0	100.0	70.5	29.5	95	5

^a The oil is not considered to be part of the actual deposit.

the oxidation of the oil. In this type of wear, the metals form metallic soaps with the organic acids.

The suspended sludge may not be visible to the naked eye; but it is precipitated from the oil when the oil is diluted with solvents, such as petroleum ether. Substances of the type of asphaltenes in the sludges are known to disperse to different degrees in oils of different types; for instance, more asphaltenes disperse in oils containing large quantities of aromatic hydrocarbons than in those containing small quantities of aromatic hydrocarbons. For this reason, drastically refined oils (aromatic type of constituents removed) retain less sludge in suspension after use than oils from the same crude oil which are mildly refined. On the other hand, the quantity of sludge-forming substances left in the oil decreases with the severity of refining. Obviously it is important to reach a proper balance in refinery operations that will insure the best oil performance. Blending of refined oils from different sources is not recommended because the mixture may not necessarily be in balance with respect to sludge formation and sludge solubility, although the individual components may be in balance. By blending refined used oils with fresh oils of a different type, the precipitation of the sludge may also be accelerated.

The dispersion of the sludge in the oil, which is one of the possible methods of preventing the sludge from depositing in the engine, may be increased by means of colloids of the so-called "protective" type. Such colloids may be present in the oil itself, or they may be added to the oil.

The discussion above is confined to lubricating oils and their stability in engines. However, lubricating oils are not the only factors responsible for engine deposits. The quality of the gasoline used must also be considered. Traces of fuel which do not undergo complete combustion may cause some of the deposit, either directly or indirectly, by affecting the stability of the lubricating oil.

Many of the problems associated with the performance of lubricating oils can be solved by automotive engineers, and closer cooperation between the automotive and refining industries is desirable. For example, piston ring wear and scuffing may be remedied or reduced by applying proper coating to the rings. Such coatings may be chemical in nature (Ferrox, an iron oxide;²⁰ Granoseal, and iron-manganese phosphate; Graphitox and Grafotox, a zinc-iron phosphate with colloidal graphite; Sulfide, a ferrous sulfide) or metallic in nature (electrically deposited tin).⁴⁶ Corrosion in engines may be alleviated or prevented by using suitable alloys, etc.

Pure lubricating oils, *i.e.*, oils derived directly from petroleum to which no addition agents have been added, have probably attained substantially the maximum degree of improvement that may normally be expected from the so-called "subtractive" refining, although it is possible, of course, that still better selection of crude oils and still further improvements in present refining methods may produce oil of better quality. Optimum conditions of refining vary with the individual properties required for the oil as evaluated by engine tests. For instance, a certain degree of refining is necessary to produce an oil that will not cause the piston rings of the engine to stick, an important specification for airplane engine oils; and after this optimum degree of refining is reached, further refining may increase the tendency of the rings to stick. The optimum degree of refining for one quality may differ from that for another quality, and a compromise of various factors must be made in the selection of the optimum degree of refining.

ADDITION AGENTS

It is known that certain deficiencies in lubricating oils which cannot be overcome by further refining can be corrected by supplying certain chemical addition agents. Many addition agents have been developed during the last few years; they have been described in recent treatises on lubricating oils.^{14, 33}

The kind of addition agent to be used depends on the quality desired to be imparted to or accentuated in the oil. Some of the agents may be beneficial under one set of operating conditions and harmful under another; also the effect of addition agents varies with the type of engine. For instance, calcium dichlorostearate is effective in preventing sticking of piston rings in Diesel engines, but it has not proved satisfactory for airplane engines.

The addition agents consist of oxidation inhibitors, oiliness carriers, viscosity index improvers, fluorescence improvers, and pour-point depressants. They are described briefly below. For further discussion of the development of these agents and for an extensive bibliography of the original lit-

erature, the reader is referred to "Modern Methods of Refining Lubricating Oils," by Kalichevsky.³³

Oxidation Inhibitors for Lubricating and Similar Oils

As pointed out previously, the mechanism of deterioration of lubricating oils in service is complex. The oils in contact with the metallic parts of engines may deteriorate much more rapidly than when subjected to similar service conditions in containers with inert surfaces.¹⁶ This effect suggests two possible methods of correction: the development of chemicals of the true oxidation inhibitor type, and the development of substances which could form a protective coating on the metal surfaces of the engines and thus eliminate or greatly reduce the catalytic action of the surfaces. The first type of substances would protect the oil in the absence of metals, and the second type in the presence of metals. Obviously substances possessing both characteristics are also possible. Substances of the first type are commonly referred to as oxidation inhibitors, and those of the second type as corrosion inhibitors.

The inhibitors first proposed for protecting lubricating oils from oxidation were: hydroxy compounds, such as phenolic derivatives and naphthols; nitrogen compounds, such as naphthylamines, aniline, and its derivatives; and sulfur compounds, represented by elemental sulfur, disulfides, etc. The list was soon extended to include compounds of the organo-metallic type and compounds of chlorine, as well as the derivatives of phosphorus, arsenic, antimony, selenium, and tellurium.

The causes of the degradation of oils in use were first intensively studied in the turbine and transformer oils, and addition agents were first added to these oils.

Stadnikov and Vozzhinskaya³¹ investigated many insulating oils and found traces of sulfonic acids in most of them. If sulfonic acids are present, the oil darkens on heating. In laboratory tests for traces of sulfonic acid, this darkening can be intensified by the addition of small percentages of acetaldehyde and acetic acid and heating.

Butkov⁹ has shown that traces of soaps in transformer oils may be conducive to rapid deterioration of the oils. Yamada³⁰ has investigated the effect of metallic soaps of naphthenic acids on the oxidation of oils and reports that 2 per cent of copper, iron, manganese, silver, cobalt, and cerium naphthenates causes much sludging when added to a switch oil (not highly refined) and heated for 100 hours at 248° F., but that calcium, barium, mercury, potassium, magnesium, and tin soaps of the same acids have an antisludging action. The addition of 0.1 per cent of the tin naphthenate is sufficient to resist sludge formation and color change, and at the same time it does not impair the electrical resistance of the oil. Tuichinir and Ivanov³⁵ also report that naphthenic salts of potassium, sodium, lithium, iron, or manganese increase the oxidizability of an acid-treated oil in tests made at 302° F. for three hours with oxygen at 15 atmospheres pressure.

In tests which Petrov and co-workers⁴⁴ made at 302° F. for 40 hours in air with the naphthenate soaps of copper, zinc, lead, and manganese, the maximum acceleration was shown by manganese, and the zinc soap was second in activity. The manganese naphthenate was more active than the sulfo-acid salt of the same metal.

Butkov⁵ increases the stability of an acid-treated oil by removing the last traces of the acid constituents with silica gel.

Morton⁴² retards oxidation of mineral lubricating oils in use in an automobile engine by the addition of a derivative of hydrogenated glyoxaline, such as 1,3-diphenyl-2-propyl-tetrahydroglyoxaline.

Von der Heyden and Typke²⁴ report that substances of a weakly basic nature, such as magnesium oxide, have an inhibiting action on the oxidation of transformer oils. This effect may be due indirectly to magnesium soaps, such as magnesium naphthenate. Traces of magnesium and calcium oleates and naphthenates dissolved in lubricating oils are known to protect them against chemical change in storage.

According to Rodman and Maude,⁴⁵ inert gases or those with reducing properties have a continuous preservative effect on transformer oils.

Protection of the oil is claimed to be furnished by "Agerite" (aldol- α -naphthylamine). The electrical resistivity of a protected oil is much higher after prolonged heating than that of an unprotected oil. "Agerite" is said to be used in the production of "Ohmoil."¹

I. G. Farbenindustrie A.-G. has patented³⁰ as inhibitors for protecting lubricating and insulating oils the following substances: hexamethylenetetramine, trioxymethylene, urca, biuret, piperidine, aldehyde-ammonia, aminoguanidine, diphenylguanidine, diethyl-aniline, hydroquinone, aminophenol, hydroxyquinoline, phenylenediamine, toluhydroquinone, and phloroglucinol.

Kaagebehn³² claims special advantages for 0.2 to 0.5 per cent of hydroxybiphenyls, such as 4-hydroxybiphenyl, for inhibiting the autoxidation of mineral oils, particularly transformer oils.

Butkov⁸ made experiments with 1 per cent of beta-naphthol for inhibiting the autoxidation of transformer oils. He continued the tests for two hours at 302° F. with oxygen under 225 pounds pressure. Table 111 compares the results obtained with and without the inhibitor.

Table 111. Inhibiting Action of 1 Per Cent of β -Naphthol on Transformer Oil for 2 Hours at 302° F. Oxygen Supplied at 225 Pounds Pressure.

	With 1% β -Naphthol	Without Inhibitor
Acid Number	0.35	16.76
Saponification Number	2.06	38.26
Soluble in H ₂ SO ₄ (%)	3.00	23.00

Butkov⁷ has also determined that beta-naphthylamine and anthracene in addition to the beta-naphthol are antioxygens for highly refined transformer and insulating oils. The oxidation tests were made at 302° F. with oxygen at 225 pounds pressure but for four hours or longer. Butkov reports that naphthalene is almost inert or may even promote the oxidation of these oils, and that phenol is inert. Aniline inhibits for 60 hours; but after that time, the acidity of the oil begins to increase rapidly. Antioxygenic properties are shown by aromatic hydrocarbons containing two or more rings, with the exception of naphthalene.

Corrosion Inhibitors

Inhibitors of the second type, or corrosion inhibitors, are a relatively recent development. They comprise various kinds of organo-metallic compounds, compounds of phosphorus, arsenic, and antimony.³³ Illustrative examples of these inhibitors of corrosion are here described.

"Santolube 31" * belongs to the phosphite ester class of corrosion inhibi-

* Santolube 31 and Santolube 36 were developed by the Socony-Vacuum Oil Company and are manufactured by the Monsanto Chemical Company.

tors and is a phosphite ester of an alkyl phenol. It is a crystalline solid at normal temperature and melts at 120-130° F. It is highly soluble in mineral oils and is recommended for protecting cadmium-silver and copper-lead bearings, especially in solvent-refined lubricating oils. In the proportion of 0.25 per cent by weight of the oil, it has no measurable effect on the physical properties of oils with the minor exception of viscosity, as indicated in Table 112.

"Santolube 36" is an organic compound of phosphorus but not a phosphite ester. It is used in concentrations as low as 0.05 to 0.10 per cent and, like "Santolube 31," has no appreciable effect on the physical properties of the oil with the exception of a slight increase in viscosity.

A solvent-refined Pennsylvania oil was tested in a single-cylinder Delco engine under accelerated conditions. The effect on the viscosity and on the bearings with and without inhibitors is shown in Table 112.

Table 112. Effect of Inhibitors on Viscosity of Oils and on Suppression of Corrosion of Alloy Bearings.

	Viscosity of Unused Oils, Saybolt Universal Seconds		Loss of Cadmium- Silver Bearings in Penn. Oil, S.A.E. 20, for 20 Hours (mg.)	Loss of Copper- Lead Bearings in Penn. Oil, S.A.E. 60, for 40 Hours, (mg.)
	100° F.	210° F.		
Oil without inhibitor	561	67.8	721	1073
Oil + Santolube 31, 0.25%	566	68.0	114	391
Oil without inhibitor	561	67.8	1046	1119
Oil + Santolube 36, 0.1%	565 ^a	68.7 ^a	39	7

^a The amount of inhibitor used in this sample was 0.2 per cent.

Oiliness Carriers

The tenacity with which a given oil is capable of adhering to the metal at high bearing pressures is commonly referred to as "oiliness." This property of the oil is usually defined as that property which accounts for a difference in the coefficient of friction in two lubricants, having the same viscosity at the temperature of the test, when used under identical conditions.²³

Oiliness is generally the same for all straight mineral oils irrespective of the nature of the crude oil or of the treating method. The observed differences are, as a rule, of little practical significance. Vegetable or animal oils, however, possess considerably greater oiliness than mineral oils. Nevertheless, for normal service, in which the bearing pressures do not exceed 2,000 pounds per square inch and rubbing speeds are high, the oiliness of the mineral oils is ample to protect the moving parts of the engine; for heavy loads or during the break-in periods, the performance of the mineral oils may be greatly improved by suitable oiliness agents.

Addition agents for improving oiliness of lubricating oils usually include small amounts of vegetable or animal oils, various derivatives of organic acids, such as esters, halogenated organic derivatives, and sulfur compounds. Various oiliness agents are discussed in the literature,^{10, 14, 33} and further references may be found among the supplementary patents.

It should be noted that in many respects a lubricating oil which contains an oiliness agent resembles the high-pressure lubricants that are used for extremely high bearing pressures, as in automobile gears. However, the oils bearing the oiliness agents are much milder than the high-pressure lubricants, which contain powerful addition agents that possess distinctly corrosive properties.

Viscosity Index Improvers

The viscosity index is a measure of the viscosity-temperature relationship of petroleum oils. For best performance, the viscosity of an oil should change as little as possible with change in temperature in order to insure free flow of oil through the engine at all times; it is particularly important to maintain good lubrication during warm-up periods in engines used intermittently. For engines in continuous service, such as turbines, the viscosity index of the oil is of minor importance; the time intervals at which the engines are run at other than normal operating temperatures are negligible.

Dean, Bauer, and Berglund¹⁵ have developed comprehensive tables which permit a quick estimate of the viscosity index of petroleum oils from known viscosities at 100 and 210° F.

It is generally known that the viscosity of a blend of oils at any given temperature is lower than the arithmetical average of the viscosity of the components at that temperature, although the effect is not so great for viscosities at higher temperatures. These divergencies of viscosities of the blends from the arithmetical average of the components at the two temperatures are in the direction that produce higher viscosity indices than indicated by the arithmetical averages of the component oils. The above and similar considerations have led to the development of the so-called viscosity index improvers—very high molecular weight substances which, when added in small proportions to an oil, favorably affect the viscosity index. It is important, however, that these complex addition agents do not dissociate at higher temperatures.

Agents for improving the viscosity index usually consist of high molecular weight polymers of unsaturated hydrocarbons, although other high molecular organic substances can be used; Calkins,¹¹ however, questions whether sufficient stability of such materials has as yet been established. Typical of the commercial addition agents now sold as viscosity index

improvers or of the oil containing them are "Uniflow," "Exanol," "Paraton," etc.

Fluorescence Improvers

The color and fluorescence of lubricating oils have no relation to their performance in engines. The same generalization applies to light petroleum products. However, the refiner is sometimes obliged at extra expense to refine the oils to meet the demand for the customary light-colored oils, even though the quality of the oil may be impaired by the additional treatment.

Fluorescence may create a deception in the actual degree of deterioration of a lubricating oil, especially after the oil has been in use for a time. Highly fluorescent oils are usually inspected in reflected and not in transmitted light, with the result that the condition of the main body of the oil escapes observation. In service, oils tend to develop black carbonaceous material, which remains at least partially suspended in them. If the oil is fluorescent and is examined in reflected light, these black particles are concealed, and the oil appears relatively unchanged. When the non-fluorescent oils are examined in transmitted light, these black particles are distinctly visible and give the impression that the oil has rapidly deteriorated in service. Actually, however, the fluorescent oil may contain considerably larger quantities of carbonaceous materials and may have deteriorated to a much larger extent than the non-fluorescent oil.

Several dyes have been developed for imparting the desired fluorescence to lubricating oils. However, the dyes designed for commercial use should be thoroughly investigated to insure their stability under service conditions; many dyes decompose in service.

The addition of fluorescent agents is not absolutely necessary for imparting to oils the yellowish-green bloom characteristic of Pennsylvania oils. Sufficient improvement frequently may be obtained by contacting oils with clay at elevated temperatures, by treating oils with sulfuric acid in propane solution, or by other conventional refining methods.

Pour-Point Depressants

The lack of fluidity in lubricating oils at moderately low temperatures (high pour point) is explained by the presence of wax, which congeals when the oil is cooled.

Asphalt is sometimes responsible for the high pour points of oils, especially the residual stocks; the pour point then cannot be lowered by dewaxing. If the pour point is affected both by asphalt and by wax, deasphalting and dewaxing operations are necessary to insure fluidity of the oil at low temperatures.

Fluidity of the oil containing wax depends not only on the quantity of wax but also on the type of wax crystals dispersed in the oil. Certain

chemicals modify the structure of the wax crystals and alter the fluidity of the oil. Such pour-point depressants may be present in the oil itself or may be added to it.

Asphaltic substances in the oil sometimes act as pour-point depressants. Oils containing both wax and asphalt may, therefore, have a higher pour test after than before deasphalting. However, asphalt cannot be tolerated in refined oils because of its unfavorable effect on the oil in service.

Several synthetic compounds have been found which, when added in small proportions to an oil, reduce the pour point. These compounds, which are high molecular weight condensation products, are represented by "Santopour," developed by the Socony-Vacuum Oil Company, Inc., and "Parafflow," developed by the Standard Oil Development Company. Such compounds are usually added to the oil in quantities of 0.5 per cent by weight or less to obtain the desired pour point.

"Santopour" is made by first condensing phenol and chlorinated wax by means of aluminum chloride and further condensing this reaction product with phthalyl chloride. "Parafflow" ¹³ is a synthetic hydrocarbon made by condensing a high-boiling monochloroparaffin with naphthalene by means of anhydrous aluminum chloride.

The data of Table 113 show the effect of small quantities of "Santopour" in depressing the pour point of two different lubricating oils.

Table 113. Effect of Pour Point Depressant on Lubricating Oil.

	Motor Oil, S.A.E. 20		Motor Oil, S.A.E. 30	
	Without Depressant	+0.16% "Santopour"	Without Depressant	+0.16% "Santopour"
Gravity (°A.P.I.)	26.8	26.8	25.8	25.8
Viscosity (Saybolt Universal Seconds, 100° F.)	325	325	570	570
Viscosity (Saybolt Universal Seconds, 210° F.)	53.3	53.3	65.2	65.2
Viscosity Index	94	94	89	89
Pour Point (°F.)	+20	-30	+20	-15
Color, A.S.T.M.	6	6	7	7
Carbon Residue (%)	0.4	0.4	0.8	0.8
Sligh Oxidation Number	9	9	8	8

The effect of two different pour-point depressants in lowering the pour point of a Mid-Continent oil is illustrated in Table 114.

Table 114. Effect of Different Amounts of Two Pour-Point Depressants on the Pour Point of a Mid-Continent Lubricating Oil.

Pour Point (°F.)	Quantity of Pour Point Depressant Added (%)	
	Depressant A	Depressant B
20	0.000	0.000
10	0.009	0.020
0	0.020	0.046
-10	0.040	0.090
-15	0.056	0.124

The property of pour-point depressants to modify the structure of the wax crystals is sometimes utilized in dewaxing operations to facilitate the separation of the wax from the oil, as noted in the chapter on Refining with Solvents.

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Supplementary List of United States Patents on Petroleum Refining

The patents listed in this section have not been discussed in the main part of the text and are here segregated in accordance with Chapters II to XI inclusive which discuss refining methods. The first division below pertains to treatment with sulfuric acid, and the second division to disposal of sulfuric acid sludge, etc. The patents of each division are arranged chronologically. Additional patents reviewed by Kalichevsky in "Modern Methods of Refining Lubricating Oils" are omitted.

CHAPTER II. TREATMENT WITH SULFURIC ACID.

- U. S. 11,203, June 27, 1854. A. Gesner. Light distillates are treated with sulfuric acid in contact with manganese dioxide.
- U. S. 32,705, July 2, 1861. J. Merrill. Treatment of oil with acid sludge, or partly spent sulfuric acid.
- U. S. 36,419, Sept. 9, 1862. A. Meucci. Petroleum distillates are treated with nitrogen peroxide.
- U. S. 45,007, Nov. 15, 1864. W. Adamson. Apparatus for treating oils with acid and alkalis.
- U. S. 57,727, Sept. 4, 1866. J. Jann. Gasoline, sweet oil, and sulfuric acid are mixed, and the separated layer is decanted and used as a burning oil.
- U. S. 59,751, Nov. 20, 1866. H. K. Taylor and D. M. Graham. Oil is treated with air and hydrogen chloride.
- U. S. 105,038, July 5, 1870. T. H. Burridge. Apparatus for treating oils with liquids and gases.
- U. S. 106,915, Aug. 30, 1870. G. Chevrier. Sulfuric acid sludge is separated from the oil by the use of sodium and aluminum chlorides.
- U. S. 127,446, June 4, 1872. J. Young. Petroleum oils are refined with hydrochloric acid.
- U. S. 139,009, May 20, 1873. J. J. Looney. Heavy crudes are treated with sulfuric acid in naphtha solution and distilled.
- U. S. 146,405, Jan. 13, 1874. E. Schalk.

- Petroleum distillates are treated with sulfuric acid and ammonia.
- U. S. 211,762, Jan. 28, 1879. T. Marrin. Treatment of paraffin distillate with sludge acid or partly spent acid.
- U. S. 299,167, May 27, 1884. J. Roswell. Treating oil with a solution of potassium nitrate and sulfuric acid.
- U. S. 336,941, Mar. 2, 1886. J. W. Norton and F. H. Rouse. Apparatus for injecting gases or chemicals into the oil during distillation.
- U. S. 495,124, Apr. 11, 1893. A. Spiegel. Mineral oils are treated with sulfuric acid to produce sulfonated compounds.
- U. S. 498,588, May 30, 1893. C. Toppan. Oils are treated with gases evolved from a mixture of sodium chloride, zinc, and sulfuric acid.
- U. S. 547,329, Oct. 1, 1895. F. X. Byerley. Crude oil is blown with air during distillation, and the distillate is treated with sulfuric acid and with sodium hydroxide solution.
- U. S. 559,783, May 5, 1896. A. Müller-Jacobs. Artificial musk is prepared by treating kerosene with sulfuric and nitric acids, neutralizing with sodium hydroxide and precipitating the odorous substances with metallic soaps.
- U. S. 596,437, Dec. 28, 1897. W. A. Smith. Oil is heated with turpentine or resin before it is treated with sulfuric acid and alkalis.
- U. S. 604,515, May 24, 1898. J. Bragg. Petroleum oils are treated with manganese or lead oleate or colophionate

- and then refined with sulfuric acid and alkalis.
- U. S. 611,620, Oct. 4, 1898. C. B. Forward and J. M. Davidson. Petroleum is treated with sulfuric acid, heavy oil is added, and the mixture is heated to prepare asphalt.
- U. S. 623,066, April 11, 1899. F. Berg. Crude petroleum is distilled in the presence of alkalis, the distillate is treated with sulfuric acid and neutralized, redistilled, and again treated with acid.
- U. S. 901,411, Oct. 20, 1908. E. W. Wynne. Petroleum is refined with borax, alum, and sodium chloride solution and then treated with sulfuric acid.
- U. S. 1,092,448, Apr. 7, 1914. M. Melamid. Decolorizing and deodorizing oils by distilling in the presence of phosphoric acid.
- U. S. 1,185,747, June 6, 1916. J. N. Wingett. Motor fuel is produced by distilling a mixture of kerosene, toluene, and nitric acid.
- U. S. 1,295,308, Feb. 25, 1919. J. O. Handy. Lubricating oils are treated with clarifying and decolorizing agents, dehydrated with dry clays, refined with sulfuric acid, and neutralized.
- U. S. 1,339,727, May 11, 1920. J. W. Trotter. Kerosene fraction of petroleum is treated with fuming sulfuric acid at 125° F., and the gasoline fraction is washed with sodium hydroxide solution.
- U. S. 1,395,968, Nov. 1, 1921. S. P. Miller. Solvent naphtha is refined with aluminum chloride, sulfuric acid, and other reagents.
- U. S. 1,416,291, May 16, 1922. A. Hayes. Motor fuel is prepared by passing a mixture of hydrocarbon vapors and alcohol through a heated catalyst containing alumina.
- U. S. 1,436,214, Nov. 21, 1922. G. Teichner. Mineral oils are treated with sulfuric acid and then oxidized in contact with catalysts.
- U. S. 1,448,084, Mar. 13, 1923. T. F. Ott. Lubricating oils are treated in several stages with sulfuric acid.
- U. S. 1,464,851, Aug. 14, 1923. S. P. Miller and J. B. Hill. Solvent naphtha is treated with sulfuric acid, aluminum chloride, or similar reagents.
- U. S. 1,475,259, Nov. 27, 1923. L. duP.
- Clement. Motor fuel is prepared by agitating a mixture of kerosene, toluene, naphtha, aluminum sulfate, sulfuric acid, and potassium bichromate.
- U. S. 1,521,282, Dec. 30, 1924. S. H. Diggs. Oils are treated with sulfuric acid and neutralized with lime.
- U. S. 1,521,283, Dec. 30, 1924. S. H. Diggs. Oils are treated with sulfuric acid and then with fuming acid without intermediate removal of the sludge.
- U. S. 1,528,327, Mar. 3, 1925. J. Hancock. Oil is atomized with steam, and a chemical is injected into the mixture before heating it to cracking temperatures.
- U. S. 1,540,929, June 9, 1925. S. P. Coblenz and S. P. Coleman. Treating an oil with 66° acid, washing with an aqueous sodium chloride solution, and breaking the emulsion with electric current.
- U. S. 1,592,058, July 13, 1926. J. W. Weir. Lubricating oils are treated with sulfuric acid and contact clays.
- U. S. 1,617,201, Feb. 8, 1927. H. N. Dons. Emulsions are avoided by neutralizing sulfuric acid-treated oils with cellulose impregnated with sodium hydroxide solution.
- U. S. 1,636,946, July 26, 1927. F. W. Weber. Crude oil is treated in succession with calcium hypochlorite, sodium peroxide, sulfuric acid, colloidal ferric chloride containing basic chlorides of rare metals, and sodium silicate, and distilled.
- U. S. 1,649,384, Nov. 15, 1927. H. Blumenberg, Jr. Deodorizing and decolorizing cracked gasoline with aluminum chlorosulfate.
- U. S. 1,703,158, Feb. 26, 1929. J. M. McClave. Oils are distilled in the presence of manganese dioxide and hydrochloric acid.
- U. S. 1,703,838, Feb. 26, 1929. C. Fischer, Jr., and W. T. Reddish. Sulfonation of mineral oils and extraction of sulfonates.
- U. S. 1,707,506, Apr. 2, 1929. H. E. Buc. Preparation of soluble sulfonates from petroleum oils.
- U. S. 1,725,320, Aug. 20, 1929. M. J. Trumble. Hydrocarbon vapors are mixed with hydrogen chloride, sulfuric

- acid, or other chemicals before they are cracked or hydrogenated.
- U. S. 1,739,898, Dec. 17, 1929. E. W. Gard, G. B. Aldridge, and H. J. Multer. Separation of finely divided, or "peppery," sludge from oil treated with sulfuric acid by filtration through porous material.
- U. S. 1,742,021, Dec. 31, 1929. A. H. Ackerman. Anthracene or naphthalene are added to lubricating oils before treatment with sulfuric acid.
- U. S. 1,767,886, June 24, 1930. T. Hellthaler, Jr. Bleaching montan wax with sodium bichromate or similar oxidizing agents in the presence of sulfuric acid.
- U. S. 1,772,921, Aug. 12, 1930. J. Tausz. Separating undesirable oil fractions which are responsible for poor color, odor, or gum in the gasoline, by fractionation.
- U. S. 1,786,650, Dec. 30, 1930. J. M. Goodwin. Oil tar from cracking operations is stabilized by treatment with 0.5-1.5% sulfuric acid of 30-60° Bé. at 200-275° F.
- U. S. 1,804,743, May 12, 1931. H. H. Cannon. Apparatus for removing acid sludge from oil by settling in shallow channels.
- U. S. 1,813,642, July 7, 1931. H. G. Smith. Removing taste and odor from petrolatum by treating with aluminum chloride and with dilute sulfuric acid.
- U. S. 1,839,114, Dec. 29, 1931. J. C. Morrell. Cracked distillates are refined with a mixture of acetic and phosphoric acids.
- U. S. 1,853,920, Apr. 12, 1932. J. C. Morrell. Cracked distillates are refined first with phosphoric acid and then with sulfuric acid.
- U. S. 1,853,921, Apr. 12, 1932. J. C. Morrell. Cracked distillates are refined with a solution of sulfur dioxide in sulfuric acid.
- U. S. 1,854,417, Apr. 19, 1932. J. C. Morrell. Sulfur compounds and polymerizable constituents are removed from cracked distillates by refining with a solution of sulfur dioxide in sulfuric acid of 95% per cent strength or higher.
- U. S. 1,855,203, Apr. 26, 1932. J. Robinson. Turbine oil is produced by refining a lubricating oil distillate with about 2-3 lbs. of concentrated sulfuric acid per barrel.
- U. S. 1,856,141, May 3, 1932. D. D. Stark. Sludge from sulfuric acid treatment is separated from the oil by passing the mixture through an aluminous abrasive filter plate. The filter plate is cleaned occasionally by washing with water.
- U. S. 1,856,700, May 3, 1932. J. G. Ford. Transformer oil is prepared by treating a suitable distillate with 15-50% by volume of 95-98% sulfuric acid.
- U. S. 1,858,394, May 17, 1932. S. H. Diggs, J. M. McGee and T. S. Cooke. Oils are desulfurized by treating the distillates which have an end point not less than 3° nor more than 20° C. above that of the desired finished product with sulfuric acid followed by redistillation to the desired end point.
- U. S. 1,864,583, June 28, 1932. G. B. Coumbrough. Petroleum vapors are washed countercurrently with water to refine them.
- U. S. 1,865,001, June 28, 1932. R. T. Goodwin. Tar containing alkalies and obtained in cracking oils in the presence of alkalies is stabilized by treatment with a small quantity of sulfuric acid.
- U. S. 1,867,814, July 19, 1932. C. Ellis. Cracked distillates are treated with nitric and sulfuric acids and then with zinc to form amino compounds, which impart antiknock properties to these distillates.
- U. S. 1,870,063, Aug. 2, 1932. J. C. Morrell. Cracked gasoline is treated with a mixture of concentrated sulfuric acid and anhydrous acetic acid.
- U. S. 1,872,679, Aug. 23, 1932. L. P. Chebotaref. Light petroleum distillates are decolorized with sulfuric acid, neutralized with sodium hydroxide solution, and then washed with sodium bicarbonate solution.
- U. S. 1,873,728, Aug. 23, 1932. C. R. Wagner. Different fractions of light petroleum distillates are segregated and treated individually with sulfuric acid of varying strengths to remove the undesirable constituents.
- U. S. 1,876,702, Sept. 13, 1932. R. I. Lewis. Pressure distillate is desulfurized with sulfuric acid at -7° C. and then treated with an additional quantity

- of sulfuric acid at room temperature before redistilling.
- U. S. 1,886,261, Nov. 1, 1932. E. B. Miller and G. C. Connolly. Light petroleum distillates are treated with 0.1-0.5% of strong sulfuric acid and, after removing the sludge, they are contacted with silica gel at 150° F. or higher.
- U. S. 1,896,470, Feb. 7, 1933. K. T. Steik. Apparatus for refining oils with sulfuric acid applied as a mist.
- U. S. 1,897,582, Feb. 14, 1933. J. C. Morrell and G. Egloff. Cracked petroleum distillates are refined in the vapor phase with sulfur trioxide and ferric sulfate in the presence of steam.
- U. S. 1,901,228, Mar. 14, 1933. L. L. Davis, A. Henriksen and J. J. Allinson. Crude petroleum oils are desalted by agitating with water at elevated temperatures and settling.
- U. S. 1,907,318, May 2, 1933. S. E. Campbell. Light petroleum distillates are treated in multistage contact with sulfuric acid of about 50% strength.
- U. S. 1,908,616, May 9, 1933. E. Petty. Oil is mixed with sulfuric acid, the sludge separated by centrifuging, the acid-treated oil contacted with adsorbents, and the spent acid recovered for reuse.
- U. S. 1,908,923, May 16, 1933. J. A. Schaeffer and G. Pfersch. Apparatus for treating oils with sulfuric acid in an atomized state.
- U. S. 1,908,924, May 16, 1933. J. A. Schaeffer and G. Pfersch. Apparatus for treating oils with atomized sulfuric acid. The sludge is separated by centrifuging.
- U. S. 1,911,419, May 30, 1933. A. N. Belcher and D. B. Nutt. Separating finely divided sulfuric acid sludge from oil by passing the mixture through crushed rock.
- U. S. 1,924,855, Aug. 29, 1933. J. B. Heid. Cracked gasoline is purified by passing its vapors successively through sulfuric acid and sodium hydroxide solutions.
- U. S. 1,927,823, Sept. 26, 1933. L. L. Davis and G. L. Atkinson. Oils are oxidized with air prior to sulfuric acid refining.
- U. S. 1,927,853, Sept. 26, 1933. C. W. Stratford. Oil is treated in several stages with acid, and the sludge is separated between the stages by centrifuging.
- U. S. 1,929,489, Oct. 10, 1933. W. W. Gary. Oils are treated with sulfur trioxide, the bulk of the sludge is settled out, and the remainder is removed by treatment with sulfuric acid.
- U. S. 1,930,249, Oct. 10, 1933. J. C. Morrell. Refining oils in the vapor phase with a mixture of fresh sulfuric acid and the sulfuric acid sludge produced in the process and containing ammonium sulfate and sulfonic acids.
- U. S. 1,932,655, Oct. 31, 1933. C. L. Erickson. Apparatus for refining oils with acid, alkali, or sodium plumbite solutions.
- U. S. 1,933,748, Nov. 7, 1933. J. C. Morrell. Refining cracked distillates with nitrogen oxides diluted with nitrogen or carbon dioxide followed by refining with sulfuric acid.
- U. S. 1,935,160, Nov. 14, 1933. J. C. Morrell. Refining cracked gasolines in the vapor phase with sulfur trioxide and steam in the presence of metals, such as zinc, tin, calcium, magnesium, aluminum, copper, lead, mercury, cobalt, nickel, chromium, manganese, molybdenum, vanadium, or tungsten.
- U. S. 1,935,161, Nov. 14, 1933. J. C. Morrell. Refining cracked distillates in the vapor phase with sulfur trioxide and steam in the presence of iron oxide.
- U. S. 1,935,162, Nov. 14, 1933. J. C. Morrell. Apparatus for refining cracked gasoline in the vapor phase with sulfuric acid.
- U. S. 1,935,207, Nov. 14, 1933. M. Har-der and W. Dietrich. Gas oil, paraffin oils, and other crude hydrocarbon materials are purified by simultaneous treatment with sulfuric acid and an oxide of nitrogen.
- U. S. 1,936,210, Nov. 21, 1933. E. Retailiau. Cracked distillates are treated with strong sodium hydroxide solution, washed with water, treated with sulfuric acid of 15-30% strength, retreated with sulfuric acid of 75-85% strength, and neutralized.
- U. S. 1,938,094, Dec. 5, 1933. S. E. Campbell. Light hydrocarbon distillates are decolorized by passing them successively through a dilute sulfuric

- acid solution, sodium hydroxide solution, and a concentrated sulfuric acid.
- U. S. 1,938,629, Dec. 12, 1933. J. Kochan. Refining residual oils with sulfuric acid.
- U. S. 1,939,129, Dec. 12, 1933. E. B. Miller and G. C. Connolly. Light hydrocarbon distillates are refined with sulfuric acid and then heated under pressure to remove further quantities of polymerizable materials.
- U. S. 1,941,266, Dec. 26, 1933. J. C. Morrell and G. Egloff. Cracked distillates are refined in the vapor phase with sulfur trioxide and steam in the presence of iron oxide.
- U. S. 1,941,267, Dec. 26, 1933. J. C. Morrell. Cracked distillates are refined in the vapor phase with a mixture of sulfuric and acetic acids.
- U. S. 1,941,970, Jan. 2, 1934. L. Caldwell. Cracked distillates are treated with sulfuric acid, neutralized, and distilled with steam over magnesium oxide. The condensate is then treated with sodium plumbite solution.
- U. S. 1,942,062, Jan. 2, 1934. A. Kemper. Oil is mixed with sulfuric acid of 60-65° Bé., and water is added to the mixture in a quantity greater than that of the acid. The acid solution is then separated from the oil.
- U. S. 1,943,583, Jan. 16, 1934. G. C. Connolly and A. F. Wurzbacher. Cracked distillates are treated with sulfuric acid at slightly elevated temperatures, the principal portion of the sludge is separated, and the remaining sludge is removed by steaming.
- U. S. 1,946,094, Feb. 6, 1934. J. C. Morrell and G. Egloff. Cracked distillates are refined with sulfur trioxide and steam by passing the mixed vapors over fuller's earth.
- U. S. 1,946,131, Feb. 6, 1934. R. F. Davis. Cracked distillates are refined by contacting their vapors with dry sulfur trioxide.
- U. S. 1,949,786, Mar. 6, 1934. S. J. Dickey. Gasoline is treated with sulfuric acid, heated to decompose the sulfonates, and immediately contacted with solid sodium hydroxide.
- U. S. 1,950,739, Mar. 13, 1934. J. C. Morrell. Hydrocarbon oils are refined with sulfuric acid containing at least 8% of barium, calcium, or sodium sulfate, glycerol, alcohol, or acetic acid.
- U. S. 1,950,878, Mar. 13, 1934. R. E. Burk. Lubricating oils are treated with chlorosulfonic acid and neutralized with contact clays.
- U. S. 1,951,647, Mar. 20, 1934. T. S. Cooke. Apparatus for separating sulfuric acid sludge from oil.
- U. S. 1,952,694, Mar. 27, 1934. K. M. Watson. Apparatus for refining hydrocarbon vapors with acid.
- U. S. 1,954,886, Apr. 17, 1934. J. C. Morrell. Cracked distillates are treated in the vapor phase with sulfuric acid containing sodium sulfate.
- U. S. 1,954,887, Apr. 17, 1934. J. C. Morrell. Cracked distillates are treated with a mixture of sulfuric acid and ammonium persulfate.
- U. S. 1,957,840, May 8, 1934. R. I. Lewis. Cracked distillates are treated with sulfuric acid first at 72° F., then at 38° F., or below, and then again at 72° F.
- U. S. 1,959,712, May 22, 1934. A. E. Flowers. Apparatus for refining lubricating oils with sulfuric acid.
- U. S. 1,962,181, June 12, 1934. G. Egloff. Apparatus for refining cracked distillates under pressure with sulfuric acid.
- U. S. 1,962,204, June 12, 1934. J. C. Morrell. Cracked distillates are treated in the vapor phase with a solution of sulfuric acid containing benzenesulfonic acid, acetic acid, chloroacetic acid, aliphatic carboxylic acid, such as oxalic or tartaric acid, or an aromatic or hydroaromatic acid, such as benzoic or terephthalic acid, or salts of such acids.
- U. S. 1,963,555, June 19, 1934. J. C. Morrell. Cracked distillates are treated with sulfuric acid containing sodium acid sulfate and sodium permanganate.
- U. S. 1,965,031, July 3, 1934. G. C. Connolly. Cracked distillates are freed from gum-forming constituents by treating with acid, adding water in quantity at least equal to that of the acid without removing the sludge, separating the oil, neutralizing the oil with alkalis, and distilling.
- U. S. 1,965,828, July 10, 1934. D. L. Fox. Separating nitrogen bases from petroleum with dry gaseous sulfur dioxide.
- U. S. 1,966,010, July 10, 1934. R. T. Howes. Separation of finely divided

- sulfuric acid sludge from the oil by filtering through opaline silica.
- U. S. 1,967,172, July 17, 1934. J. C. Morrell. Cracked distillates are refined with sulfuric acid containing hydrogen fluoride, hydrogen bromide, or hydrogen iodide.
- U. S. 1,969,316, Aug. 7, 1934. J. C. Morrell. Cracked distillates are refined in the vapor phase with sulfuric acid of 10-60% strength and containing an alkaline or alkaline-earth sulfate.
- U. S. 1,973,118, Sept. 11, 1934. C. F. Spencer. Cracked residuum is treated with sulfuric acid and clay in naphtha solution to produce substances which impart green bloom to lubricating oil.
- U. S. 1,973,119, Sept. 11, 1934. C. F. Spencer. Cracked residuum is treated in naphtha solution with sulfuric acid and sodium carbonate and contacted with clay to produce substances which impart green bloom to petroleum oils.
- U. S. 1,973,621, Sept. 11, 1934. F. X. Govers. Lubricating oils are treated with sulfuric acid, neutralized with sodium carbonate solution, the resulting emulsion is resolved with calcium or magnesium hydroxides, and the oil contacted with clay.
- U. S. 1,974,170, Sept. 18, 1934. C. R. Baker. Lubricating oils are treated with sulfuric acid, washed with a water-soluble sulfonic acid, and heated with a decolorizing clay.
- U. S. 1,975,987, Oct. 9, 1934. C. W. Stratford. Countercurrent treatment of gasoline with sulfuric acid involving centrifugal separation of sludge and cooling between the stages.
- U. S. 1,984,903, Dec. 18, 1934. C. R. Wagner. Desalting crude oils with water at elevated temperatures.
- U. S. 1,985,717, Dec. 25, 1934. S. E. Campbell. Apparatus for refining petroleum distillates with sulfuric acid.
- U. S. 1,988,648, Jan. 22, 1935. E. F. Engelke. Lubricating oils are treated with sulfuric acid and neutralized with lime.
- U. S. 1,992,308-9, Feb. 26, 1935. E. W. Hultman. Petroleum distillates are refined with sulfuric acid of 35-80% strength which has been subjected to electrolysis.
- U. S. 1,992,420, Feb. 26, 1935. A. W. Gleason and D. B. Nutt. Apparatus for treating oils with sulfuric acid.
- U. S. 1,993,446, Mar. 5, 1935. L. C. Huff. Apparatus for treating hydrocarbon distillates with refining reagents.
- U. S. 1,994,511, Mar. 19, 1935. W. W. Gary. Refining petroleum oils with gaseous sulfur trioxide.
- U. S. 1,997,566, Apr. 16, 1935. R. E. Beard and E. N. Roberts. Revivification of spent green acid soap used for treating lubricating oils.
- U. S. 1,997,896, Apr. 16, 1935. W. S. Baylis. Residuum is treated with sulfuric acid, mixed with decolorizing clay, and fractionated.
- U. S. 1,997,980, Apr. 16, 1935. L. B. Smith. Passing sulfuric acid sludge into hot oil to effect coking of at least a portion of the sludge.
- U. S. 1,999,128, Apr. 23, 1935. F. H. MacLaren. Cracked petroleum fractions are sulfonated with sulfuric acid to obtain wetting agents.
- U. S. 2,004,849, June 11, 1935. M. E. Bretschger and E. A. Bosing. Cracked distillates are treated with hydrogen peroxide in the presence of sulfuric acid.
- U. S. 2,005,342, June 18, 1935. L. D. Jones and E. M. James. Apparatus for contacting petroleum oils with sulfuric acid in finely dispersed state.
- U. S. 2,009,878, July 30, 1935. R. T. Goodwin. Treatment of cracked fuel oil with sulfuric acid.
- U. S. 2,009,902, July 30, 1935. R. C. Osterstrom. Sulfuric acid treatment of cracked distillates, and fractionation.
- U. S. 2,013,399, Sept. 3, 1935. W. I. Benedict and C. Wirth, III. Cracked distillates are treated with sulfuric acid containing dissolved ferric chloride.
- U. S. 2,015,703, Oct. 1, 1935. N. F. Black and J. A. Tilton. Cracked gasoline is refined with 98% sulfuric acid at 35-72° F.
- U. S. 2,016,336, Oct. 8, 1935. P. W. Merchant. Apparatus for treating hydrocarbon oils with sulfuric acid.
- U. S. 2,017,610, Oct. 15, 1935. D. R. Stevens and W. A. Gruse. Cracked petroleum distillates are treated with sulfuric acid in the presence of phenol or similar substances.

- U. S. 2,018,715, Oct. 29, 1935. S. C. Fulton. Lubricating oils are treated with a mixture of 66° Bé. sulfuric acid, glacial acetic acid, and formaldehyde.
- U. S. 2,022,268, Nov. 26, 1935. F. M. Archibald and P. Janssen. Acid-treated light hydrocarbon oils are freed from sulfuric acid esters by flash distillation in the presence of previously separated esters.
- U. S. 2,023,545-6, Dec. 10, 1935. E. T. Pummill. Apparatus for countercurrent treatment of oils with sulfuric acid.
- U. S. 2,025,409, Dec. 24, 1935. J. C. Black. Distilling gasoline into fractions, followed by chemical refining of some of the fractions.
- U. S. 2,027,648, Jan. 14, 1936. J. C. Morrell. Refining cracked distillates, first with a mixture of nitric and acetic acid and then with sulfuric acid.
- U. S. 2,029,115, Jan. 28, 1936. J. C. Morrell. Vapor phase treatment of cracked distillates with sulfuric acid containing a sulfonated aromatic hydrocarbon.
- U. S. 2,029,785, Feb. 4, 1936. J. C. Morrell. Cracked distillates are refined in the vapor phase with a mixture of sulfuric and phosphoric acids.
- U. S. 2,031,939, Feb. 25, 1936. T. R. Donlan. Apparatus for treating oils with fuming sulfuric acid or sulfur trioxide at above 175° F.
- U. S. 2,032,662, Mar. 3, 1936. J. M. McGee and R. M. Roe. Gasoline is fractionated, and the different fractions are treated with various quantities of sulfuric acid and recombined.
- U. S. 2,033,145, Mar. 10, 1936. J. C. Morrell. Cracked distillates are distilled, and the light and heavy fractions treated separately before reblending.
- U. S. 2,035,349, Mar. 24, 1936. H. G. Smith. Lubricating oil is treated with sulfuric acid, the sludge is separated, and the oil further deacidified by heating to elevated temperatures.
- U. S. 2,035,655, Mar. 31, 1936. L. D. Jones. Continuous treatment of cylinder stocks with sulfuric acid and separating the sludge by centrifuging.
- U. S. 2,036,299, Apr. 7, 1936. J. Robinson. Recovery of acid from sulfuric acid sludge by extraction with amyl alcohol.
- U. S. 2,038,369, Apr. 21, 1936. E. G. M. R. Légé. Treatment of petroleum oils by injecting them at 300-575° F. into a large quantity of 48-65° Bé. sulfuric acid.
- U. S. 2,041,754, May 26, 1936. W. W. Gary. Refining oils with a mixture of sulfuric acid and oil previously recovered from acid sludge.
- U. S. 2,043,936, June 9, 1936. L. G. Story. Refining oils with sulfuric acid at a pressure of 300-3000 pounds per square inch.
- U. S. 2,045,234, June 23, 1936. J. C. Morrell. Refining cracked distillates in the vapor phase with a mixture of sulfuric acid, sodium acid sulfate, and a chromate.
- U. S. 2,047,985, July 21, 1936. H. M. Weir. Controlling a continuous acid treating process by means of a photoelectric cell.
- U. S. 2,048,521, July 21, 1936. J. H. Shepard. Lubricating oil is treated with sulfuric acid, neutralized with ammonia, and extracted with Chlorex.
- U. S. 2,049,016, July 28, 1936. J. C. Morrell. Refining cracked distillates in the vapor phase with sulfuric acid containing aniline.
- U. S. 2,050,345, Aug. 11, 1936. L. Libberthson. Refining lubricating oils with fuming sulfuric acid followed by extraction with Chlorex.
- U. S. 2,055,416, Sept. 22, 1936. F. R. Moser. Cracked distillates are refined in the vapor phase with benzenesulfonic acid.
- U. S. 2,060,835, Nov. 17, 1936. C. W. Stratford and A. E. Drissner. Apparatus for centrifugal separation of sulfuric acid sludge from the oil.
- U. S. 2,062,377, Dec. 1, 1936. H. G. Schneider. Refining cracked distillates with boron fluoride in sulfuric acid.
- U. S. 2,062,733, Dec. 1, 1936. G. J. Strezynski. Oils are treated with sulfuric acid and neutralized with a solution of sodium hydroxide containing sodium metasilicate and triethanolamine.
- U. S. 2,066,200, Dec. 29, 1936. W. A. Eberle and M. B. Hopkins. Lubricating oils are treated with 66° Bé. sulfuric acid and percolated through fuller's earth while still in the acid state.
- U. S. 2,068,847, Jan. 26, 1937. G. H. B. Davis and J. I. Wasson. Separation of

- fine sludge by washing the oil with sulfuric acid of 50% strength, or higher, in the presence of toluene.
- U. S. 2,073,253, Mar. 9, 1937. G. M. Pfau, D. C. Bolin, and E. W. Zublin. Apparatus for refining heavy lubricating oils with sulfuric acid.
- U. S. 2,076,581, Apr. 13, 1937. M. S. Kharasch. Refining gasoline with anhydrous hydrogen fluoride.
- U. S. 2,079,443, May 4, 1937. S. C. Fulton. Refining cracked distillates with concentrated or fuming sulfuric acid at -22 to $+150^{\circ}$ F. in two stages.
- U. S. 2,080,701, May 18, 1937. R. B. Day. Refining cracked distillates in the liquid phase with hydrochloric acid and then in the vapor phase with copper and zinc.
- U. S. 2,080,732, May 18, 1937. J. C. Morrell. Gasoline is refined in the vapor phase with sulfuric acid containing benzaldehyde or acetophenone.
- U. S. 2,083,253, June 8, 1937. I. Budowski. Refining hydrocarbon distillates with chromates and sulfuric acid.
- U. S. 2,085,527, June 29, 1937. S. M. Gregory. Refining cracked distillates with sulfuric acid and manganese dioxide.
- U. S. 2,085,545, June 29, 1937. E. R. P. E. Retailliau. Separating fine sulfuric acid sludge from oils with acetone.
- U. S. 2,088,216, July 27, 1937. E. R. P. E. Retailliau. Acid treated oil is freed from last traces of acid by heating with water under pressure.
- U. S. 2,088,406, July 27, 1937. F. M. Clark. Refining mineral oils with a mixture of sulfuric and phosphoric acid.
- U. S. 2,088,500, July 27, 1937. H. I. Waterman. Treating oils with acetylene in the presence of aluminum chloride.
- U. S. 2,093,645, Sept. 21, 1937. W. J. Podbielniak. Apparatus for refining oils with sulfuric acid or other reagents by counterflowing them in a spiral rotating passage of increasing diameter.
- U. S. 2,099,529, Nov. 16, 1937. R. C. Moran and W. A. Meyer. Extraction of sulfonic acids from acid-treated oils.
- U. S. 2,099,835, Nov. 23, 1937. E. H. Barlow, A. P. Hewlett, and P. E. Kuhl. Naphtha is fractionated, and the individual fractions are separately refined before reblending.
- U. S. 2,107,713-4, Feb. 8, 1938. H. R. Rowland and E. J. Smith. Refining gasoline with sulfuric acid and then with chlorine.
- U. S. 2,109,446, Feb. 22, 1938. M. T. Kendall. Fractionating kerosene fraction, and separately treating the individual fractions with sulfuric acid before reblending.
- U. S. 2,111,548, Mar. 22, 1938. M. L. Berry. Refining residual stocks with sulfuric acid in the presence of isopentane or isoöctane to improve sludge separation.
- U. S. 2,114,352, Apr. 19, 1938. A. A. Neff. Acid-treated lubricating oils are neutralized by heating them to elevated temperatures.
- U. S. 2,116,208, May 3, 1938. G. J. Malherbe. Cracked distillates are treated with sulfuric acid sludge formed in refining straight-run distillates.
- U. S. 2,119,240, May 31, 1938. W. E. Lyons. Storing uninhibited gasolines over solutions of boric or lactic acids or monosodium phosphate.
- U. S. 2,120,135, June 7, 1938. C. E. Lauer and L. V. Phillips. Lubricating oils are treated with sulfuric acid and heated to elevated temperatures to remove the fine sludge. The heated oil is then distilled.
- U. S. 2,121,167, June 21, 1938. L. U. Franklin. Gasoline is treated with sulfuric acid after diluting it with gasoline already treated with acid.
- U. S. 2,122,059, June 28, 1938. D. K. Harger and H. I. Wolff. Acid-treated lubricating oils are heated to elevated temperatures to remove the last traces of sludge.
- U. S. 2,123,503, July 12, 1938. E. M. Dons and D. B. Mapes. Heavy lubricating oil is treated with sulfuric acid, diluted with a lighter lubricating oil distillate, and the blend treated again with sulfuric acid.
- U. S. 2,126,867, Aug. 16, 1938. N. Brewer. Refining white oils with sulfuric acid.
- U. S. 2,129,751, Sept. 13, 1938. A. A. Wells and D. F. Edwards. Centrifugal separation of sludges from oils.
- U. S. 2,131,879, Oct. 4, 1938. W. C. Ault and C. A. Hochwalt. Catalytic refining

- of motor fuels in the vapor phase with phosphoric acid.
- U. S. 2,133,452, Oct. 18, 1938. A. P. Hewlett. Refining kerosene with sulfuric acid in the presence of boron fluoride.
- U. S. 2,133,457, Oct. 18, 1938. N. E. Lemmon. The acid-treated oil is washed with alcohol, treated with sodium hydroxide solution, again washed with alcohol, and contacted with fuller's earth.
- U. S. 2,140,161, Dec. 13, 1938. E. J. Martin. Dewaxed oil is treated with sulfuric acid at not above 0° F.
- U. S. 2,141,622, Dec. 27, 1938. H. B. Setzler. Still residue is added to a lubricating oil distillate, the mixture is chilled to separate the wax, and then treated with sulfuric acid. Wax and sludge are removed simultaneously.
- U. S. 2,142,359, Jan. 2, 1939. E. R. Lederer and G. M. Pfau. Simultaneous dewaxing and refining of lubricating oils with sulfuric acid at below 0° F.
- U. S. 2,142,998, Jan. 10, 1939. M. B. Chittick. High pressure lubricants are prepared by heating mineral oils with phosphoric anhydride.
- U. S. 2,143,531, Jan. 10, 1939. A. P. Anderson. Sulfuric acid refining of solvent-treated oils in the presence of small quantities of the solvent extract to facilitate separation of sludge.
- U. S. 2,143,890, Jan. 17, 1939. L. Liberthson. Treating lubricating oils with fuming sulfuric acid in Chlorex solution.
- U. S. 2,145,025, Jan. 24, 1939. R. M. Isham and H. N. Lyons. Treating cracked benzine with sulfuric acid below 60° F. for alcohol and sweet gasoline.
- U. S. 2,145,784, Jan. 31, 1939. A. P. Anderson and E. J. Jahn. Refining paraffin wax with sulfuric acid.
- U. S. 2,145,852, Feb. 7, 1939. W. H. Bahlke. Refining lubricating oils with propane followed by sulfuric acid.
- U. S. 2,150,084, Mar. 7, 1939. A. L. Tammchill. Gasoline is distilled, the light fraction is washed with sodium hydroxide solution, and the residual fraction with sulfuric acid. The two fractions are then combined and inhibited.
- U. S. 2,153,560, Apr. 11, 1939. P. R. Hershman. Resalting and demulsifying petroleum oils with glycerol solutions containing formaldehyde and naphthenic acids, or their soaps, and sulfonated derivatives.
- U. S. 2,154,424, Apr. 18, 1939. C. E. Dolbear. Refining cracked distillates with sulfuric acid followed by neutralization with calcium oxide and blowing with air in the presence of sodium ferrite.
- U. S. 2,155,007, Apr. 18, 1939. T. O. Edwards, Jr., and D. D. Stark. Counter-current refining of light distillates with sulfuric acid at low temperatures.
- U. S. 2,157,315, May 9, 1939. F. M. Archibald. Removing ash-forming constituents from lubricating oils with dilute sulfuric acid.
- U. S. 2,158,690, May 16, 1939. S. E. Campbell. Apparatus for refining oils with sulfuric acid.
- U. S. 2,162,992, June 20, 1939. W. C. Ault and C. A. Hochwalt. Removing gum-forming constituents by passing gasoline vapors through liquid acids of phosphorus.
- U. S. 2,166,502, July 18, 1939. O. H. Milmore. Lubricating oil is treated with sulfuric acid, and the sludge precipitated in the presence of methane or ethane dissolved in the oil under pressure.
- U. S. 2,166,503, July 18, 1939. O. H. Milmore. Lubricating oil is treated with sulfuric acid, and the sludge is precipitated by dissolving carbon dioxide or methyl fluoride in the oil under pressure.
- U. S. 2,170,336, Aug. 22, 1939. J. C. Morrell. Refining gasoline vapors with sulfuric acid containing chloroacetic or sulfanilic acid.
- U. S. 2,170,620, Aug. 22, 1939. C. Skrepinsky. Refining lubricating oils at elevated temperature by first contacting with air and then refining with sulfuric acid.
- U. S. 2,174,908, Oct. 3, 1939. W. C. Ault and C. A. Hochwalt. Refining cracked distillates by heating in the liquid phase with phosphoric acid.
- U. S. 2,176,196, Oct. 17, 1939. C. M. Beamer and J. Hooton. Refining hydrocarbon vapors with sodium hydroxide, sulfuric acid, and sodium sulfide solutions.

- U. S. 2,177,734, Oct. 31, 1939. C. P. McNeil. Refining lubricating oils successively with sulfuric acid and sodium hydroxide in propane solution.
- U. S. 2,185,577, Jan. 2, 1940. A. Voorhies, Jr., and E. E. Stahly. Gasoline containing olefinic polymers is desulfurized with sulfuric acid of 45-75% strength.

CHAPTER III.—SULFURIC ACID SLUDGE AND HYDROGEN SULFIDES: MANUFACTURE OF SULFURIC ACID.

- U. S. 160,759, Mar. 16, 1875. L. S. Fales and P. Neff. Recovering and purifying oil from acid sludge.
- U. S. 178,061, May 30, 1876. W. P. Jenney. Treatment of oil recovered from acid sludge by agitation with steam in the presence of caustic soda and lead or manganese oxide.
- U. S. 178,154, May 30, 1876. W. P. Jenney. Preparation of resins from acid sludge.
- U. S. 206,309, July 23, 1878. F. F. Farrar and E. P. Gill. Treatment of acid sludge with hot water to separate the oil.
- U. S. 306,897, Oct. 21, 1884. R. M. Breining. Sulfuric acid sludge is treated with soap to recover the acid which is further deodorized with lime.
- U. S. 315,597, Apr. 14, 1885. R. M. Breining. Sulfuric acid sludge is treated with soap to recover the acid.
- U. S. 495,343, Apr. 11, 1893. E. Jacobson. Sulfonic acids are prepared by heating oil with sulfur.
- U. S. 518,990, May 1, 1894. H. A. Frasch. Sulfonic acids are prepared by treating mineral oils with sulfuric acid.
- U. S. 625,332, May 23, 1899. L. O. Helmers. Sulfonated compounds obtained in treating petroleum oils with sulfuric acid are oxidized and concentrated by heating.
- U. S. 643,578, Feb. 13, 1900. W. Waring and J. E. Breckenridge. Oxidation of organic matter in sludge acid with sodium nitrate.
- U. S. 671,135, Apr. 2, 1901. L. O. Helmers. Preparation of sulfonic acids and their salts.
- U. S. 709,321, Sept. 16, 1902. L. O. Helmers. Sulfonic acids are separated from the oil by means of aniline or other organic bases.
- U. S. 722,506, Mar. 10, 1903. L. O. Helmers. Method of preparing metallic sulfonates.
- U. S. 722,507, Mar. 10, 1903. L. O. Helmers. Preparation of salts of oxidized sulfonic acids.
- U. S. 956,184, Apr. 26, 1910. G. Schildhaus and C. Condrea. Recovery of oil and sulfur dioxide from acid sludge by heating to 390-660° F., passing air heated to the same temperature through the sludge, and condensing some of the oil, etc.
- U. S. 956,276, Apr. 26, 1910. L. Blacher and S. Sztencel. Apparatus for concentrating sulfuric acid.
- U. S. 1,005,425, Oct. 10, 1911. E. B. Gray. Apparatus for concentrating sulfuric acid.
- U. S. 1,010,221, Nov. 28, 1911. J. S. Blowski and A. A. Blowski. Decomposing sludge acid in the presence of air to destroy the organic matter.
- U. S. 1,063,025, May 27, 1913. A. Gellen. Apparatus for concentrating sulfuric acid.
- U. S. 1,063,870, June 3, 1913. J. Goepper and O. Geiger. Heating oil with sulfuric acid to produce resinous material.
- U. S. 1,092,386, Apr. 7, 1914. W. Pan and P. Eberhardt. Recovery of resinous products by extracting sulfuric acid sludge with an aromatic hydrocarbon.
- U. S. 1,196,274, Aug. 29, 1916. G. Petrov. Preparation of soaps from acid sludges.
- U. S. 1,210,725, Jan. 2, 1917. D. Tyrer. Petroleum sulfonates are formed by heating the oil with sulfuric acid at below 392° F.
- U. S. 1,211,721, Jan. 19, 1917. L. Landsberg. Making various by-products from acid sludge.
- U. S. 1,231,985, July 3, 1917. C. Baskerville. Separation of asphaltic material from sludge acid by heating and then neutralizing the resin with lime.
- U. S. 1,232,109, July 3, 1917. J. V. Skoglund. Apparatus for concentrating sulfuric acid (Geyser Action process).
- U. S. 1,263,950, Apr. 23, 1918. W. A. Slater. Separation of sulfuric acid from acid sludge by diluting with water or weak acid. The separated acid is

- concentrated by countercurrent treatment with hot air.
- U. S. 1,276,822, Aug. 27, 1918. J. Stewart. Neutralizing alkaline sludge with sodium acid sulfate and recovering the oily material.
- U. S. 1,375,506, Apr. 19, 1921. E. D. Gray. Separation of sulfonic acids from oil by centrifuging.
- U. S. 1,438,101, Dec. 5, 1922. R. E. Divine. Sulfonic acids are precipitated as aluminum soaps from which the acids are recovered by treatment with sulfuric acid.
- U. S. 1,477,829, Dec. 18, 1923. E. M. Johansen. Sulfonic acids are prepared by treating cracked distillates with sulfuric acid.
- U. S. 1,535,656, Apr. 28, 1925. G. Egloff. Recovery of oil and sulfuric acid from acid sludge.
- U. S. 1,539,246, May 26, 1925. J. B. Edwards and F. E. Faulkner. Concentration of recovered sulfuric acid.
- U. S. 1,621,071, Mar. 15, 1927. W. D. Kinkade and C. J. Baugh. Separation of oil suitable for fuel from acid sludge by incomplete neutralization of acid sludge with lime and sodium hydroxide.
- U. S. 1,636,724, June 26, 1927. A. A. Vineyard. Separation of oil from sludge acid by diluting with water and heating.
- U. S. 1,642,060, Sept. 13, 1927. L. Burgess. Separation of oil from acid sludge with a saturated sodium chloride solution at 120° F.
- U. S. 1,673,045, June 12, 1928. E. D. Gray. Preparation of a demulsifying agent from petroleum sludges.
- U. S. 1,682,369, Aug. 28, 1928. J. M. Cory and F. H. Bunke. Preparation of liquid fuel from acid sludge by mixing the sludge with spent clay and a fluxing material, such as oil, in the presence of steam or other suitable heating agent.
- U. S. 1,682,713, Aug. 28, 1928. E. W. Roth. Separation of oil from acid sludge.
- U. S. 1,780,205. Nov. 4, 1930. H. F. Maurel. Briquets from acid sludge.
- U. S. 1,838,030, Dec. 22, 1931. M. D. Mann, Jr., and A. Holmes. Acid sludge from oils treated with sulfur trioxide is heated to 170-260° F. to decompose it into volatile products containing sulfur dioxide and a residuum containing sulfuric acid.
- U. S. 1,844,513, Feb. 9, 1932. O. Mantius. Reclaiming weak acid from acid sludge by concentrating first in the absence of air, then in the presence of air to oxidize organic material, and then again in the absence of air.
- U. S. 1,862,060, June 7, 1932. F. R. Moser and J. Greutert. Acid sludge from lubricating oil refining is mixed with an equal quantity of petroleum asphalt preheated to 248° F. or higher, and the mixture further heated to about 480° F.
- U. S. 1,878,933, Sept. 20, 1932. J. J. Lawton. Acid sludge is mixed with an inert oil, and the mixture is distilled, leaving a fluid residue.
- U. S. 1,896,583, Feb. 7, 1933. C. O. Hoover. Sludge is removed from lubricating oils with a dry mixture of fuller's earth and calcium hydroxide or carbonate in quantities insufficient to neutralize the acid oil completely.
- U. S. 1,901,383, Mar. 14, 1933. G. Voogt. Oil-soluble sulfonic acids are recovered by separating the sulfuric acid sludge, adding to the oil an alcoholic alkali solution, treating the alcoholic extract with sodium chloride, and extracting the remaining oily mixture with alcohol.
- U. S. 1,909,587, May 16, 1933. J. Kuhl and W. H. Shiffier. Sludge from refining hydrocarbon oils with aluminum chloride is converted into gas and coke by contacting with gases relatively free from oxygen.
- U. S. 1,917,869, July 11, 1933. J. C. Bird. Resins are prepared by heating the sulfuric acid sludge and treating it with sodium chlorate.
- U. S. 1,919,664, July 25, 1933. D. R. Merrill and P. S. Clarke. Sludges from refining light petroleum distillates with sulfuric acid and which tend to emulsify with water are extracted with water containing some sulfuric acid, and heated.
- U. S. 1,920,787, Aug. 1, 1933. E. J. Hammers and E. Eichwald. Separation and purification of sulfonic acids from sulfuric acid sludges.
- U. S. 1,929,675, Oct. 10, 1933. M. L. Chappell and E. F. Baker. Sulfuric

- acid sludge is burned and converted into sulfur dioxide.
- U. S. 1,930,488, Oct. 17, 1933. K. S. Ramayya. Sulfonic acid salts are purified by dissolving them in aqueous alcohol and agitating the solution with gasoline.
- U. S. 1,933,070, Oct. 31, 1933. S. Pilat. Sulfonates are recovered by neutralizing the sulfuric acid sludge with lime and treating the sulfonates with sodium carbonate solution.
- U. S. 1,935,666, Nov. 21, 1933. K. S. Ramayya. Green petroleum sulfonic acids are freed from sulfuric acid and mixed with not over 30% of mahogany acids to obtain a stable emulsifying agent.
- U. S. 1,945,172, Jan. 30, 1934. W. S. Wilson. Sludge acid is diluted with water, and the separated water solution is contacted with calcined clay.
- U. S. 1,947,861, Feb. 20, 1934. L. Libberthson. Preparation of water-soluble sulfonates from sulfuric acid sludges.
- U. S. 1,956,592, May 1, 1934. K. S. Ramayya. Petroleum sulfuric acid sludges are extracted with ethyl alcohol solutions.
- U. S. 1,958,630, May 15, 1934. H. Limburg. Emulsifying agents from sulfuric acid sludges.
- U. S. 1,960,348, May 29, 1934. E. von Pongratz. Sulfuric acid sludge is immediately diluted with water and filtered.
- U. S. 1,960,828, May 29, 1934. W. T. Reddish and L. D. Myers. Recovery of sulfonates from fuming sulfuric acid sludges by extraction with ethyl alcohol.
- U. S. 1,975,131, Oct. 2, 1934. H. W. Thompson and J. T. Rutherford. Hydrolyzing sulfuric acid sludge with steam and water.
- U. S. 1,976,528, Oct. 9, 1934. P. O. Vandever. Sulfuric acid sludge is burned in admixture with fuel oil.
- U. S. 1,981,799, Nov. 20, 1934. H. E. Buc. Purification of petroleum sulfonates with iso-propyl alcohol and potassium carbonate.
- U. S. 1,983,678, Dec. 11, 1934. J. T. Rutherford. Separation of oil from sulfuric acid sludge by heating.
- U. S. 1,987,278, Jan. 8, 1935. W. S. Wilson. Hydrolyzing sulfuric acid sludge with water and steam.
- U. S. 1,989,512, Jan. 29, 1935. W. Glaser. Production of aluminum sulfate from sulfuric acid sludge.
- U. S. 1,996,692, Apr. 2, 1935. W. von Piotrowski and J. Winkler. Sulfuric acid sludge is hydrolyzed with water and sodium hydroxide solution, the oily layer is distilled, and the residue is further heated to cracking temperatures in the absence of steam.
- U. S. 2,003,640, June 4, 1935. J. A. Wunsch. Production of naphthenates from sulfuric acid sludges.
- U. S. 2,005,309, June 18, 1935. Geo. Armistead. Preparation of cracked motor fuels from sulfuric acid sludges.
- U. S. 2,014,556, Sept. 17, 1935. J. W. Chewning and W. C. Dickerman, Jr. Sulfuric acid sludge is mixed with fuel oil and heated to remove the acid and to render the mixture suitable for fuel.
- U. S. 2,022,800, Dec. 3, 1935. A. B. Brown and D. W. Bransky. Spent acid is treated with "oleum liver" and water and heated to facilitate separation of oily constituents.
- U. S. 2,025,401, Dec. 24, 1935. J. T. Rutherford. Manufacture of ammonium sulfate and denaturants from sulfuric acid sludges.
- U. S. 2,028,185, Jan. 21, 1936. J. C. Bird. Extraction of sulfuric acid sludge with iso-propyl alcohol.
- U. S. 2,035,106, Mar. 24, 1936. H. G. Vesterdal and E. W. Carlson. Purification of sulfonates with alcohol or acetone solutions.
- U. S. 2,036,469, Apr. 7, 1936. E. Field. Manufacture of sulfonic acids from kerosene.
- U. S. 2,036,973, Apr. 7, 1936. F. W. Sullivan, Jr. Heating the acid sludge and treating the carbonaceous material with hydrogen to produce lubricating oils.
- U. S. 2,038,559, Apr. 28, 1936. S. R. Funsten. Sulfuric acid is recovered by spraying the sludge beneath a water surface.
- U. S. 2,041,957, May 26, 1936. A. Reis. Oil is recovered by neutralizing sulfuric acid sludge with alkaline material and distilling.

- U. S. 2,043,646, June 9, 1936. W. H. Bahlke. Recovery of sulfur dioxide, hydrocarbons, and coke from acid sludge.
- U. S. 2,062,347, Dec. 1, 1936. F. M. Archibald. Recovery of oil and acid from sulfuric acid sludge.
- U. S. 2,064,549, Dec. 15, 1936. C. E. Lauer, R. E. Manley, and H. D. Loeb. Production of fuel oil from sulfuric acid sludge.
- U. S. 2,065,617, Dec. 29, 1936. H. W. Sheldon. Recovery of sulfuric acid from sludge, and its fortification.
- U. S. 2,068,149, Jan. 19, 1937. L. D. Myers and L. A. Stegemeyer. Recovery of sulfonic acids from sulfuric acid sludges.
- U. S. 2,074,061, Mar. 16, 1937. E. J. Mullen. Preparation of sulfur dioxide by combustion of acid sludge.
- U. S. 2,078,882, Apr. 27, 1937. R. L. Savage, Jr. Preparation of fuel oil from sulfuric acid sludge.
- U. S. 2,079,424, May 4, 1937. C. L. Read and P. J. Harrington. Sulfuric acid is recovered by mixing sludges obtained from refining heavy and light oils and diluting the mixture with water.
- U. S. 2,086,733, July 13, 1937. E. J. Mullen. Recovery of sulfur dioxide from sulfuric acid sludge.
- U. S. 2,092,200, Sept. 7, 1937. W. H. Bahlke. Cracking sulfuric acid sludge.
- U. S. 2,097,271, Oct. 26, 1937. C. P. Debuch and E. Markworth. Burning of sulfuric acid sludge for the recovery of sulfur dioxide.
- U. S. 2,097,440, Nov. 2, 1937. M. Blumer. Purification of sulfonic acid soaps.
- U. S. 2,111,920, Mar. 22, 1938. A. A. Wells. Acid sludge is stabilized by diluting it with water.
- U. S. 2,121,845, June 28, 1938. E. A. Wernicke. Preparation of sulfonates from mineral oils.
- U. S. 2,125,936, Aug. 9, 1938. L. Liberthson. A tin mahogany sulfonate is added to lubricating oils to prevent corrosion.
- U. S. 2,168,315, Aug. 8, 1939. M. Blumer. Purification of petroleum sulfonates.

CHAPTER IV.—TREATMENT WITH ALKALINE REAGENTS.

- U. S. 22,727, Jan. 25, 1859. E. N. Horner. Distillates are treated with a mixture of cream of tartar, sodium chloride, and lime.
- U. S. 32,885, July 23, 1861. S. M. Mott. Lubricating oils are treated with sodium chloride, potassium nitrate, lime, common soap, and steam.
- U. S. 43,325, June 28, 1864. J. Merrill. Hydrocarbon distillates are treated with sodium sulfate and sodium hydroxide.
- U. S. 54,192, Apr. 24, 1866. L. M. Mott. Oil is distilled in the presence of sodium chloride, lime, potassium nitrate, and potassium hydroxide.
- U. S. 54,267, Apr. 24, 1866. J. Fordred. Crude oil is washed with sodium hydroxide or potassium hydroxide solutions.
- U. S. 74,756, Feb. 25, 1868. G. W. Flow-ers, J. C. Happersett, and D. W. Happersett. Gasoline is distilled in the presence of sodium chloride, iodine, and lime.
- U. S. 81,093, Aug. 18, 1868. J. A. Kestler. Lubricating oils are treated with sodium carbonate solution.
- U. S. 96,097, Oct. 26, 1869. A. Farrar. Residuum is washed with sodium hydroxide solution and distilled over lime.
- U. S. 174,291, Mar. 21, 1876. C. L. Morehouse. Oils are steamed, washed with sodium hydroxide solution, and filtered.
- U. S. 228,392, June 1, 1880. T. J. F. Regan. Naphtha is treated with lime.
- U. S. 336,941, Mar. 2, 1886. J. W. Norton and F. H. Rouse. Apparatus for treating oils with alkalis in the course of distillation.
- U. S. 507,441, Oct. 24, 1893. H. Koehler. Petroleum vapors are passed through lime.
- U. S. 596,410, Dec. 28, 1897. O. Lugo. Treating oils by heating with sodium aluminate solution.
- U. S. 716,132, Dec. 16, 1902. J. S. Stewart-Wallace and W. B. Cowell. Treating oil by heating it with potassium permanganate in alkaline solution.
- U. S. 732,937, July 7, 1903. C. B. Graham. Oil is refined with a solution of

- pyrogallic acid, lime, and potassium hydroxide.
- U. S. 736,479, Aug. 18, 1903. F. Berg. Oil is refined by refluxing with alkali hydroxides.
- U. S. 741,517, Oct. 13, 1903. T. Macalpine. Treating oil with a solution of sodium chloride and sodium carbonate, then with an oxidizing agent, and finally distilling in the presence of a manganese compound.
- U. S. 958,820, May 24, 1910. J. H. Parker. Petroleum is refined in the vapor phase with a mixture of lime, coke, sodium chloride, ferric oxide, and calcium borate.
- U. S. 962,840, June 28, 1910. J. J. Hood and A. G. Salamon. Decolorizing oils by filtration through magnesium oxide.
- U. S. 1,073,233, Sept. 16, 1913. R. Hense. Motor fuels are prepared by fractional distillation of a mixture of heavy and light hydrocarbons, sodium hydroxide, resin, and picric acid.
- U. S. 1,081,801, Dec. 16, 1913. S. Wohle. Petroleum oils are refined with saponaceous substances prepared from seaweed or quillai bark.
- U. S. 1,098,763-4, June 2, 1914. F. Richter. Treating oil with oxygen in the presence of sodium hydroxide and finely divided carbon.
- U. S. 1,111,580, Sept. 22, 1914. S. M. Herber. Oil is distilled in the presence of lime. Steam and air may be employed.
- U. S. 1,277,605, Sept. 3, 1918. H. W. Knottenbelt. Acid-treated oils are neutralized with alkaline solutions of lithium.
- U. S. 1,302,094, Apr. 29, 1919. C. J. Skidmore and P. F. Conerty. The use of trisodium phosphate to separate matter from spent lubricating oils.
- U. S. 1,313,629, Aug. 19, 1919. C. K. Francis. Hydrocarbon oils are mixed with saponaceous mixtures containing excess alkaline materials and distilled.
- U. S. 1,450,617, Apr. 3, 1923. J. Smith. Mineral oils are desulfurized by heating under pressure with cotton waste saturated with alkali.
- U. S. 1,454,593, May 8, 1923. E. E. Arnold. Mineral oils are treated with anhydrous ammonia in the presence of an oxygen-bearing compound of an alkali metal and catalysts.
- U. S. 1,480,368, Jan. 8, 1924. J. Black. Motor fuel is prepared by distilling a mixture of crude petroleum, coal oil, acetone, benzol, sodium carbonate, and wood alcohol.
- U. S. 1,520,953, Dec. 30, 1924. E. M. Johansen. Separation of oily substances of different capabilities for emulsification by subjecting them to a selective emulsifying action of soap solutions.
- U. S. 1,540,218, June 2, 1925. W. T. Maloney. Preparation of transformer oils by oxidizing with oxygen or ozone and adding sodium hydroxide to precipitate the oxidized compounds.
- U. S. 1,553,141, Sept. 8, 1925. L. H. Clark. Oils (used lubricating oils) containing finely dispersed carbon are purified by mixing them with alkalies, and centrifuging.
- U. S. 1,686,491, Oct. 2, 1928. W. S. Hughes and J. Harrop. Breaking alkaline emulsion with acid.
- U. S. 1,694,478, Dec. 11, 1928. P. F. Miller. The precipitation of extraneous matter from spent lubricating oils.
- U. S. 1,708,592, Apr. 9, 1929. W. D. Rial and W. R. Barratt. Increasing fluorescence of lubricating oils by treating with calcium hydroxide and coal tar pitch.
- U. S. 1,709,203, Apr. 16, 1929. J. C. Black, W. D. Rial, and R. T. Howes. Neutralizing lubricating oils with sodium hydroxide and adsorbents.
- U. S. 1,715,095, May 28, 1929. J. C. Morrell and H. P. Benner. Corrosion is reduced by introducing ammonia vapors during distillation.
- U. S. 1,718,714, June 25, 1929. L. Link and M. B. Anis. Removing elementary sulfur with spent alkalies.
- U. S. 1,728,156, Sept. 10, 1929. R. C. Wheeler and P. W. Prutzman. Revivifying solid sodium hydroxide used in vapor-phase refining of oils by steaming.
- U. S. 1,732,905, Oct. 22, 1929. R. A. Morgen, W. S. Yard, and L. Rosenstein. Regenerating waste sodium hydroxide solution with air in the presence of nickel sulfide as catalyst.
- U. S. 1,738,518, Dec. 10, 1929. F. C.

- Axtell. Petroleum oils are distilled in contact with sodium carbonate.
- U. S. 1,742,020-1, Dec. 31, 1929. A. H. Ackerman. Lubricating oils are treated with mixtures of naphthalene, anthracene, sodium hydroxide, phosphate rock, sugar, and oil of mirbane.
- U. S. 1,764,117, June 17, 1930. C. K. Parker. Neutralizing acid-treated oils by heating with sodium hydroxide solution under pressure.
- U. S. 1,770,181, July 8, 1930. J. C. Morrell. Residual oils are homogenized by passing between closely adjacent surfaces and under pressure with or without addition of soaps of alkali earth metals.
- U. S. 1,785,242, Dec. 16, 1930. A. E. Becker and R. G. Sloane. Recovering naphthenates, etc., from petroleum residues obtained in distilling oils in the presence of caustic soda.
- U. S. 1,787,505, Jan. 6, 1931. J. C. Black and W. D. Rial. Improving the color and demulsibility of lubricating oils from California or similar crude oils by heating at about 340° F. under pressure with potassium hydroxide solution (about 10" B.C.) prior to acid treatment.
- U. S. 1,787,570, Jan. 6, 1931. C. P. Dubbs. Removing carbon disulfide or similar compounds from cracked distillates with calcium hydroxyhydrosulfide, which may be formed from calcium hydroxide, water, and hydrogen sulfide present in the oil.
- U. S. 1,789,026, Jan. 13, 1931. F. W. Sullivan, Jr. Lowering the cold test of lubricating oils by addition of zinc or magnesium salts of acidic products derived from oxidation of paraffin.
- U. S. 1,804,451, May 12, 1931. T. M. Andrews and C. E. Lauer. Naphthene-base lubricating oil distillates are redistilled in the presence of alkalis, and the still residue which contains naphthenic acid soaps is treated with alcohol.
- U. S. 1,808,853, June 9, 1931. C. J. Livingston and W. A. Gruse. Improving lubricating oils used in automobiles by adding to them a small quantity of soap and carbon tetrachloride.
- U. S. 1,812,924, July 7, 1931. W. T. Bryant. Distilling lubricating oils in the presence of sodium hydroxide solution, treating the heavier fractions with sulfuric acid, and decolorizing with adsorbents.
- U. S. 1,827,912, Oct. 13, 1931. L. Rosenstein. Removing hydrogen sulfide from oils by contacting with a solution of sodium carbonate and sodium bicarbonate, which is regenerated by blowing with air in the presence of nickel sulfide, used as a catalyst.
- U. S. 1,833,396, Nov. 24, 1931. W. W. Gary. Oils are filtered through solid sodium hydroxide deposited on an inert material before they are treated with acid.
- U. S. 1,946,096, Feb. 6, 1934. J. C. Morrell and G. Egloff. Cracked distillates are refined by passing their vapors through a solution of borax.
- U. S. 1,859,262, May 17, 1932. J. A. Shaw. Oil treated with sulfuric acid is washed with a solution of sodium hydroxide and sodium phenolate in an amount just insufficient to neutralize the oil, followed by washing with a similar solution to complete the neutralization and to remove phenol liberated in the first washing.
- U. S. 1,867,908, July 19, 1932. D. E. Day. Naphtha is treated with sodium hydroxide solution at 350-500° F. and under pressure sufficient to prevent vaporization.
- U. S. 1,881,044, Oct. 4, 1932. H. H. Cannon. Acid-treated oil is neutralized with dry powdered sodium carbonate and dry powdered diatomaceous earth.
- U. S. 1,890,229, Dec. 6, 1932. J. C. Morrell and J. L. Essex. Hydrocarbon distillates are freed from gum-forming constituents by refining with borax at elevated temperatures and under pressure.
- U. S. 1,890,230, Dec. 6, 1932. J. C. Morrell and J. L. Essex. Hydrocarbon distillates are freed from gum-forming constituents by refining with a mixture of borax and clay at elevated temperatures and under pressure.
- U. S. 1,902,221, Mar. 21, 1933. D. E. Day. Naphtha is purified by heating with concentrated alkali solution at 350-500° F. and under pressure. Air is introduced into the mixture after the pressure is released.

- U. S. 1,903,407, Apr. 4, 1933. A. E. Pew. Hot oil containing lubricating oil fractions is treated with sodium hydroxide solution, and the water is evaporated by distributing the hot mixture over a wide surface.
- U. S. 1,904,381, Apr. 18, 1933. J. C. Morrell. Cracked distillates are refined in the vapor phase with adsorbents containing soda lime.
- U. S. 1,921,116, Aug. 8, 1933. L. Caldwell. Gasolines or lubricating oils are neutralized after sulfuric acid treatment with brucite or magnesium hydroxide in the presence of water containing magnesium sulfate.
- U. S. 1,929,933, Oct. 10, 1933. A. G. Peterkin, Jr., and L. B. Smith. Oil-wax mixtures are treated with alkaline silicate solutions at elevated temperatures to segregate various melting point materials.
- U. S. 1,929,934, Oct. 10, 1933. A. G. Peterkin, Jr., and L. B. Smith. Heated sodium silicate solutions are employed for separating waxes of high melting point from those of low melting point.
- U. S. 1,933,410, Oct. 31, 1933. S. M. Blair, F. L. Melvill, A. G. V. Berry, and B. G. Banks. Separation of various constituents from alkaline sludges.
- U. S. 1,938,513, Dec. 5, 1933. R. Brunck, A. Kreutzer, and W. Boeck. Naphthenic acids are liberated from oil residue, obtained in distilling oils over alkalis, by acidifying with sulfuric acid.
- U. S. 1,942,071, Jan. 2, 1934. C. J. Smith. Hydrogen sulfide is removed from hydrocarbon oils by washing with sodium carbonate solution, which is reactivated.
- U. S. 1,952,622, Mar. 27, 1934. L. Caldwell. Acid-treated oils are neutralized by filtering through a mixture of brucite and tripoli.
- U. S. 1,953,336, Apr. 3, 1934. S. E. Campbell. Naphthenic distillates are treated successively with sodium carbonate solution, sodium hydroxide solution, and sulfuric acid, and then neutralized.
- U. S. 1,954,116, Apr. 10, 1934. L. Caldwell. Sulfuric acid-treated oils are neutralized with powdered dolomite in the presence of water.
- U. S. 1,954,959, Apr. 17, 1934. R. K. Stratford and W. P. Doohan. Oils containing sulfur dioxide are treated with hot sodium hydroxide solution containing phenols or naphthenic acid compounds.
- U. S. 1,968,397, July 31, 1934. R. T. Howes. Acid-treated oils are neutralized with solutions containing magnesium hydroxide and magnesium sulfate.
- U. S. 1,969,694, Aug. 7, 1934. F. W. Hall. Cracked distillates treated with sulfuric acid are first neutralized with calcium carbonate and then with sodium hydroxide.
- U. S. 1,971,172, Aug. 21, 1934. W. L. Benedict. Cracked distillates containing mercaptans and alkyl disulfides are treated with oxygen and ammonia in the vapor phase, while in contact with activated carbon.
- U. S. 1,984,432, Dec. 18, 1934. J. Robinson. Acid-treated lubricating oils are neutralized by passing them into a large volume of a 2% sodium hydroxide solution.
- U. S. 1,998,765, Apr. 23, 1935. W. B. Logan. Oils containing naphthenic acids are distilled in the presence of concentrated sodium hydroxide solution.
- U. S. 1,997,670, Apr. 16, 1935. G. L. Armour. The brand of a light petroleum distillate may be identified by employing a mixture of dyes which gives a specific coloration with sodium hydroxide solution.
- U. S. 2,006,407, July 2, 1935. A. E. Pew, Jr. Treatment of crude oil before distillation with sodium hydroxide solution.
- U. S. 2,007,146, July 2, 1935. F. M. Rogers. Naphthenic acids are removed by passing oil vapors through molten and anhydrous sodium hydroxide.
- U. S. 2,020,932, Nov. 12, 1935. R. E. Burk and E. C. Hughes. Sodium hydroxide solutions containing mercaptan are purified by washing with naphtha containing elementary sulfur.
- U. S. 2,025,766, Dec. 31, 1935. B. Mead. Distilling acid-treated oils in the presence of sodium naphthenate.
- U. S. 2,029,005, Feb. 4, 1936. W. H. Beardsley. Refining lubricating oils with sodium hydroxide followed by sulfuric acid treatment and coagulation of the sludge with 1.5-3.0% by volume of water.

- U. S. 2,030,245, Feb. 11, 1936. R. H. Crosby and B. R. Carney. Refining hydrocarbon oils with lime.
- U. S. 2,034,197, Mar. 17, 1936. J. C. Morrell. Refining cracked distillates in the vapor phase with a solution of sodium hydroxide containing an alkali metal permanganate.
- U. S. 2,034,712, Mar. 24, 1936. C. E. Dolbear. Vapor phase refining of light petroleum distillates with a mixture of partially hydrated lime and sodium hydroxide.
- U. S. 2,039,106, Apr. 28, 1936. R. F. Nelson and L. Zapf. Recovery of naphthenic acids from petroleum by distilling in the presence of sodium hydroxide, emulsifying the residuum with water, adding a light oil, and acidifying the mixture with acid.
- U. S. 2,043,254, June 9, 1936. W. M. Malisoff. Refining light distillates with alcoholic solution of sodium hydroxide containing a little water and then with sulfuric acid.
- U. S. 2,045,492, June 23, 1936. A. E. Pew, Jr. Apparatus for treating residuums with sodium hydroxide.
- U. S. 2,047,475, July 14, 1936. R. T. Howes. Neutralizing acid-treated oils with magnesium hydroxide in the presence of water.
- U. S. 2,048,784, July 28, 1936. H. E. Drennan. Phenolic compounds are removed from spent alkali solutions by extraction with amyl alcohol.
- U. S. 2,053,752, Sept. 8, 1936. A. C. Vobach. Petroleum distillates are neutralized with sodium hydroxide immediately after they are condensed.
- U. S. 2,056,913, Oct. 6, 1936. H. T. Terrell, E. M. Hughes, and P. L. Carter. Naphthenic acid soaps are prepared from residues, obtained in distilling oils in the presence of alkalies, by acidifying the residues with sulfuric acid, mixing them with a light oil, distilling, and neutralizing the condensate with sodium hydroxide.
- U. S. 2,059,459, Nov. 3, 1936. B. Malishev. Cracked distillates are refined with sodium hydroxide solution and then with solid phosphorus pentoxide.
- U. S. 2,064,541, Dec. 15, 1936. P. R. Hershman. Oils are desalted by treating with a mixture of bleaching powder, a soluble chromate, sodium acid sulfate, and sodium peroxide.
- U. S. 2,074,183, Mar. 16, 1937. P. R. Hershman. Desalting petroleum oils with a mixture of sodium hydroxide, sodium acetate, alcohol, glycerol, and water.
- U. S. 2,075,871, Apr. 6, 1937. F. L. Smith. Deodorizing petroleum products with sodium hydroxide solution containing a demulsifier obtained from sulfuric acid sludge.
- U. S. 2,076,392, Apr. 6, 1937. R. Z. Williams. Haze in the light fuel oils is removed by washing with a 2-10% solution of sodium hydroxide at 165-210° F.
- U. S. 2,080,737, May 18, 1937. D. B. Nutt and J. H. Easthagen. Apparatus for removing hydrogen sulfide from oils with alkaline solutions.
- U. S. 2,081,498, May 25, 1937. D. R. Merrill. Extraction of lubricating oils with sodium hydroxide solution prior to refining with aniline, chloroaniline, or liquid ammonia.
- U. S. 2,082,787, June 8, 1937. A. E. Birch. Separation of black precipitate from sweetened gasoline distillates with sodium hydroxide solution.
- U. S. 2,091,020, Aug. 24, 1937. V. L. Shipp. Preparation of naphthenates from waste alkaline liquors by treating them with lead acetate.
- U. S. 2,093,001, Sept. 14, 1937. A. L. Blount. Recovery of naphthenic acids.
- U. S. 2,094,612, Oct. 5, 1937. W. M. Malisoff and J. H. Boyd, Jr. Removing mercaptans from petroleum distillates with a 1% sodium hydroxide solution, followed by refining with stronger alkaline solutions.
- U. S. 2,105,523, Jan. 18, 1938. C. F. Denney. Oil vapors are treated with sodium hydroxide solution injected into the cracking zone.
- U. S. 2,106,976, Feb. 1, 1938. J. M. Harris, Jr., and N. F. Black. Neutralizing acid-treated lubricating oils with ammonia at elevated temperatures.
- U. S. 2,112,313, Mar. 29, 1938. W. H. Sowers. Neutralizing organic acidity of lubricating oils with sodium hydroxide.
- U. S. 2,131,938, Oct. 4, 1938. H. J. Donker. Refining naphthenic acid with

- alkaline solutions of adjusted concentration.
- U. S. 2,133,094, Oct. 11, 1938. W. B. Hendrey. Extracting sodium naphthenates from the tar obtained in distilling oils over alkalies by diluting the tar with naphtha and washing with water.
- U. S. 2,134,390, Oct. 25, 1938. B. S. Greensfelder, M. E. Spaght, and C. H. Britten. Neutralizing sulfuric acid-treated oils with a solution of sodium hydroxide and soap.
- U. S. 2,134,547, Oct. 25, 1938. H. E. Buc. Sodium hydroxide solutions in methyl alcohol are used for extracting phenolic materials from hydrocarbon oils.
- U. S. 2,136,608, Nov. 15, 1938. A. L. Blount. Naphthenic acids are recovered from oils by washing the oils with alkali solutions containing naphthenic acid soaps.
- U. S. 2,140,194, Dec. 13, 1938. D. L. Yabroff and J. W. Givens. Sodium hydroxide solution employed for extracting mercaptans is regenerated by oxidizing it with an electric current which converts mercaptans to disulfides.
- U. S. 2,140,574, Dec. 20, 1938. C. S. Cerf. Mineral oils are desalted by percolating through rock salt.
- U. S. 2,148,056, Feb. 21, 1939. R. E. Burk and E. C. Hughes. Apparatus for refining petroleum distillates with caustic soda solutions.
- U. S. 2,151,147, Mar. 21, 1939. W. von Piotrowski and J. Winkler. Neutralizing sulfuric acid sludge with lime followed by distillation of the oil.
- U. S. 2,174,023, Sept. 26, 1939. H. G. Vesterdal. Phenolic and acid substances are extracted from spent sodium hydroxide solutions by treating them with carbon dioxide.
- U. S. 2,177,343, Oct. 24, 1939. E. C. Hughes. Desulfurizing petroleum distillates with magnesium oxide followed by washing with sodium hydroxide solution.
- U. S. 2,133,094, Oct. 11, 1938. W. B. Hendrey. Extracting sodium naphthenates from the tar obtained in distilling oils over alkalies by diluting the tar with naphtha and washing with water.
- U. S. 63,749, Apr. 9, 1867. T. Restieaux. Desulfurizing oils with mercury dissolved in nitric or hydrochloric acid.
- U. S. 63,789, Apr. 16, 1867. J. Ellis and E. C. Kattell. Desulfurizing oils by distilling with steam in the presence of steel packing.
- U. S. 110,054, Dec. 13, 1870. G. Lupton. Desulfurizing gasoline with ferric oxide, calcium oxide, barium chloride, and sodium carbonate.
- U. S. 129,014, July 16, 1872. A. Farrar. Oils are deodorized by blowing with air or steam.
- U. S. 289,788, Dec. 4, 1883. H. Ujhely. Decolorizing and deodorizing lubricating oils by treating with potassium ferrocyanide.
- U. S. 306,734, Oct. 21, 1884. L. H. Friedburg. Oils are deodorized with steam.
- U. S. 372,672, Nov. 8, 1887. T. G. Hall. Oils are desulfurized by passing their vapors mixed with steam over granite.
- U. S. 389,898, Sept. 25, 1888. R. M. Perrine. Decolorizing wax with calcium hypochlorite and steam.
- U. S. 413,187, Oct. 22, 1889. E. D. Kendall. Deodorizing oils with sulfur chloride.
- U. S. 414,601, Nov. 5, 1889. L. Stevens. Oils are desulfurized by passing their vapors mixed with steam through molten asphalt.
- U. S. 439,745, Nov. 4, 1890. E. A. Edwards. Illuminating oils are desulfurized by distilling them in contact with steam and air.
- U. S. 444,833, Jan. 20, 1891. B. N. Hawes. Desulfurizing oil vapors by passing them through gravel.
- U. S. 451,660, May 5, 1891. E. D. Kendall. Desulfurizing oils by treating with mercuric chloride and sodium sulfide solutions, followed by distillation in the presence of alkalies.
- U. S. 452,578, May 19, 1891. C. C. Mengel, Sr. Petroleum vapors are desulfurized by heating them with natural gas.
- U. S. 470,911, Mar. 15, 1892. J. A. Dubbs. Crude oils are desulfurized by agitating them with a gas rich in hydrogen prior to distillation.

CHAPTER V.—SWEETENING OPERATIONS,
ELIMINATION OF ELEMENTAL SULFUR,
AND REDUCTION IN TOTAL SULFUR IN
LIGHT DISTILLATES.

U. S. 53,656, Apr. 3, 1866. R. Newell.
Treatment of oils with alkaline solu-

- U. S. 486,406, Nov. 15, 1892. J. B. Huston. Petroleum vapors are desulfurized with steam, followed by water washing.
- U. S. 492,419, Feb. 28, 1893. T. McGowan. Desulfurizing oils by distilling in a still containing mineral wool saturated with sodium plumbite.
- U. S. 522,028, June 26, 1894. W. B. Price. Desulfurizing oils by treating with nitric and nitrous acids and nitrogen oxides, followed by distillation in the presence of sulfuric acid.
- U. S. 534,295, Feb. 19, 1895. J. J. Suckert. Desulfurizing oils by heating with metals or metal oxides.
- U. S. 537,121, Apr. 9, 1895. C. Lossen. Desulfurizing oils by heating with cuprous oxide.
- U. S. 551,941, Dec. 24, 1895. O. P. Amend and J. H. Macy. Desulfurizing oils by heating with alkalies, adding to the mixture aluminum or lead oxide.
- U. S. 556,155, Mar. 10, 1896. W. P. Lowe and C. W. Bilfinger. Mineral oils are distilled with steam to remove sulfur compounds.
- U. S. 607,017, July 12, 1898. T. F. Colin. Crude oils are desulfurized by distillation in the presence of sodium, barium, or lead peroxides.
- U. S. 620,882, Mar. 14, 1899. A. J. Boote and H. G. W. Kittredge. Desulfurizing oils with sodium plumbite solution and calcium hypochlorite.
- U. S. 640,918, Jan. 9, 1900. A. Kayser. Oil vapors are desulfurized by heating with carbon monoxide.
- U. S. 655,500, Aug. 7, 1900. T. Macalpine. Petroleum oils are desulfurized by treatment with a compound of acetylene and manganese.
- U. S. 664,677, Dec. 25, 1900. R. E. Pippig and O. F. F. Trachmann. Illuminating gas is desulfurized by scrubbing with an alcoholic solution of aniline.
- U. S. 683,354, Sept. 24, 1901. F. C. Thiele. Desulfurizing crude oil with nitric acid, followed by addition of metallic powders to produce nascent hydrogen.
- U. S. 685,907, Nov. 5, 1901. T. F. Colin. Desulfurizing oils by treating with sulfuric acid in the presence of a metal or metal oxide which has an affinity for oxygen.
- U. S. 686,663, Nov. 12, 1901. T. Macalpine. Desulfurizing oils with an acetylene compound of manganese.
- U. S. 770,214, Sept. 13, 1904. H. S. Blackmore. Petroleum oils containing sulfur are purified with metallic carbides.
- U. S. 809,087, Jan. 2, 1906. H. S. Blackmore. Oils are desulfurized with carbonyls of metals.
- U. S. 826,089, July 17, 1906. D. T. Day. Deodorization by hydrogenation in the presence of palladium black or platinum sponge.
- U. S. 837,655, Dec. 4, 1906. J. Armstrong. Deodorizing oil by treating with a solution of calcium hypochlorite, sodium bicarbonate, and potassium bichromate.
- U. S. 908,400, Dec. 29, 1908. J. E. Eggleston. Hydrogen sulfide is removed by heating the oil in a specially designed apparatus.
- U. S. 1,004,632, Oct. 3, 1911. D. T. Day. Deodorization with hydrogen in the presence of clay.
- U. S. 1,018,040, Feb. 20, 1912. J. E. Eggleston. Hydrogen sulfide is removed from petroleum oils by distillation and used for manufacturing sulfuric acid.
- U. S. 1,112,602, Oct. 6, 1914. J. Dehnst. Deodorizing oils by heating in the presence of sulfur.
- U. S. 1,205,578, Nov. 21, 1916. H. Strache and P. Porges. Desulfurizing oils by passing oil vapors over metallic oxides in the presence of steam.
- U. S. 1,274,912, Aug. 6, 1918. W. F. M. McCarty. Desulfurizing oil with steam in the presence of aluminum salts and then with hydrogen in the vapor phase and in the presence of catalysts.
- U. S. 1,277,092, Aug. 27, 1918. A. M. McAfee. Paraffin wax is refined by heating with aluminum chloride at 150° F.
- U. S. 1,277,328, Aug. 27, 1918. A. M. McAfee. Kerosene is refined by heating with aluminum chloride at 150° F.
- U. S. 1,277,329, Aug. 27, 1918. A. M. McAfee. Medicinal oils are prepared by heating with aluminum chloride.
- U. S. 1,326,072, Dec. 23, 1919. A. M. McAfee. Gasoline is treated by heating in the presence of aluminum chloride.

- U. S. 1,349,294, Aug. 10, 1920. W. B. Price and E. Dietz. Desulfurizing cracked gasoline vapors with metallic oxide.
- U. S. 1,365,894, Jan. 18, 1921. D. T. Day. Petroleum oils are treated with cuprous chloride.
- U. S. 1,409,404, Mar. 14, 1922. A. S. Ramage. Desulfurizing gasoline vapors with steam in the presence of ferric oxide.
- U. S. 1,423,711, July 25, 1922. J. C. Clancy. Desulfurizing oils by heating with liquid ammonia and an oxidizing agent, such as ammonium persulfate, in the presence of a catalyst.
- U. S. 1,428,885, Sept. 12, 1922. A. Hayes. Mixture of petroleum vapors and alcohols is passed through a heated catalyst containing nickel or zinc.
- U. S. 1,445,688, Feb. 20, 1923. E. M. Hyatt. Treatment of fuel oil with chlorine before charging to cracking still.
- U. S. 1,448,643, Mar. 13, 1923. P. von Ditmar. Desulfurizing oils with metallic soaps in the presence of sodium metal.
- U. S. 1,451,052, Apr. 10, 1923. H. Rostin. Mixture of oil vapors and hydrogen sulfide are passed over metallic copper to effect hydrogenation.
- U. S. 1,527,847, Feb. 24, 1925. A. M. Duckham and J. S. Morgan. Oils are distilled in a bath of molten metal.
- U. S. 1,536,908, May 5, 1925. J. S. Morgan. Oils are distilled in a bath of molten metal.
- U. S. 1,545,440, July 7, 1925. H. Neumann. Mineral oils are treated with a saturated solution of ferric halides.
- U. S. 1,551,806, Sept. 1, 1925. R. F. Davis. Desulfurizing oils with cupric oxide in the presence of light.
- U. S. 1,558,632, Oct. 27, 1925. H. Reinbold and H. Reinbold. Oils are refined with aluminum and lithium chlorides.
- U. S. 1,569,872, Jan. 19, 1926. J. C. Morrell. Subjecting oils to doctor treatment, and then washing with sodium sulfide solution to remove elemental sulfur.
- U. S. 1,573,370, Feb. 16, 1926. E. Blümlner. Oils are distilled in a bath of molten metal.
- U. S. 1,574,507, Feb. 23, 1926. G. G. Oberfell, A. M. Ballard, R. C. Alden, E. L. Utsinger, and W. R. Lentz. Sweetening natural gasoline by dissolving elemental sulfur therein and passing the solution through a warm sodium plumbite solution.
- U. S. 1,594,083, July 27, 1926. G. L. Wendt. Treatment of oil with doctor solution before distilling.
- U. S. 1,581,369, Apr. 20, 1926. J. W. Weir. Using lead oxide to remove sulfur dioxide from lubricating oils subjected to acid and to clay treatment. The clay treatment is made at 350° F. to break up the acid compounds and give good color.
- U. S. 1,598,973, Sept. 7, 1926. G. Kolsky. Treating the oil with ammonia in the presence of finely divided iron.
- U. S. 1,608,328, Nov. 23, 1926. A. M. McAfee. Petroleum oils are treated with hydrogen in the presence of aluminum chloride.
- U. S. 1,608,339, Nov. 23, 1926. H. M. Ridge and W. R. Hodgkinson. Desulfurizing oils with a mixture of copper, cupric oxide, and a copper halide.
- U. S. 1,609,349, Dec. 7, 1926. F. I. duPont. Oils are distilled in the presence of molten metals.
- U. S. 1,623,018, Mar. 29, 1927. R. Cross. Desulfurizing oils by treating with chlorine in sunlight.
- U. S. 1,654,581, Jan. 3, 1928. R. Cross. Treating oils with doctor solution in a countercurrent manner at above 200° F.
- U. S. 1,655,068, Jan. 3, 1928. P. McMichael. Treating oils at elevated temperatures with lime and ammonium chloride or similar reagents.
- U. S. 1,658,505, Feb. 7, 1928. G. L. Wendt. Gasoline is sweetened with alcoholic sodium plumbite solution.
- U. S. 1,685,034, Sept. 18, 1928. D. Rider. Oils are passed through molten metals before they are distilled to remove sulfur.
- U. S. 1,687,992, Oct. 16, 1928. E. B. Phillips and J. G. Stafford. Oil vapors are treated with solid cupric chloride and then with fuller's earth.
- U. S. 1,691,266, Nov. 13, 1928. L. Caldwell. Sweetening gasoline with a reagent produced by treating diatomaceous earth and lime with chlorine.

- U. S. 1,703,616, Feb. 26, 1929. G. Egloff. Cracked distillates are mixed with drying oils and distilled to effect desulfurization.
- U. S. 1,704,246, Mar. 5, 1929. R. A. Halloran. Hydrogen sulfide is removed by washing cracked distillates with water under pressure.
- U. S. 1,710,063, Apr. 23, 1929. J. C. Morrell. Treating oil with plumbite solution, distilling, blending the distillate with the residue, and redistilling.
- U. S. 1,716,973, June 11, 1929. M. G. Paulus. Oil is saturated with hydrogen sulfide before treating with sodium plumbite solution.
- U. S. 1,718,218, June 25, 1929. R. Cross. Pretreating cracking stock with sodium plumbite solution and acid.
- U. S. 1,733,656, Oct. 29, 1929. G. Egloff and J. C. Morrell. Desulfurizing petroleum distillates with metallic oxides and oxidizing agents.
- U. S. 1,744,611, Jan. 21, 1930. E. B. Phillips and J. G. Stafford. Treating oil vapors with sodium hydroxide solution containing dissolved copper oxide.
- U. S. 1,767,356, June 24, 1930. H. G. M. Fischer. Sweetening gasoline with litharge and sodium hydroxide solution while agitating with air. Sulfur is added to the oil in small quantities during the agitation.
- U. S. 1,768,683, July 1, 1930. T. T. Gray. Sweetening cracked gasoline with copper acetate and then treating it in the vapor phase with fuller's earth.
- U. S. 1,769,792, July 1, 1930. W. G. Leamon. Treating cracked gasoline with zinc chloride or aluminum chloride dissolved in ether or isopropyl alcohol.
- U. S. 1,776,752, Sept. 23, 1930. L. Edeleanu. Treatment of oil with liquid sulfur dioxide and then sweetening with sodium plumbite solution and elemental sulfur.
- U. S. 1,777,005, Sept. 30, 1930. J. L. Looney. Apparatus for treating oils with sodium plumbite or similar reagents.
- U. S. 1,778,517, Oct. 14, 1930. R. C. Benner and A. P. Thompson. Treating oils with adsorbents which have been saturated with salts of heavy metals and ignited.
- U. S. 1,786,246, Dec. 23, 1930. E. B. Hunn. Sweetening light distillates with sodium plumbite solution and propyl disulfide.
- U. S. 1,788,204, Jan. 6, 1931. W. Posth and F. Besemann. Treating oils with hypochlorite solutions in the presence of nickel, cobalt, or cupric sulfate, which accelerate the decomposition of the hypochlorites, heating to about 140° F., and separating the oil.
- U. S. 1,789,335, Jan. 20, 1931. H. G. M. Fischer and W. J. Addems. Sweetening gasoline by agitating with lead sulfide, sodium hydroxide, and sulfur.
- U. S. 1,791,179, Feb. 3, 1931. G. L. Wendt. Isolation of mercaptans from gasoline to be used for the subsequent removal of elemental sulfur in the presence of sodium plumbite by washing the oil with a sodium hydroxide solution and by treating the washings with lime to decompose sodium sulfide which may be present.
- U. S. 1,791,521, Feb. 10, 1931. A. P. Bjerregaard. Sweetening oil distillates with solid alkali hydroxides in the presence of alcohol and in absence of water.
- U. S. 1,794,668, Mar. 3, 1931. W. F. Bleeker. Removing corrosive sulfur compounds from petroleum oils with nascent chlorine produced by electrolysis of salt.
- U. S. 1,795,278, Mar. 3, 1931. H. G. M. Fischer. Gasoline is sweetened by contacting with sulfur in the presence of a catalyst, distilled under reduced pressure, and the residue heated to above 350° F. in order to reduce its sulfur content.
- U. S. 1,799,431, Apr. 7, 1931. J. C. Morrell. Desulfurization of cracked distillates by heating with zinc and glacial acetic acid.
- U. S. 1,801,412, Apr. 21, 1931. P. J. Carlisle. Desulfurization of oils in the vapor phase with metallic sodium or other alkali metals by suspending them in the reflux liquid in the fractionating column.
- U. S. 1,803,964, May 5, 1931. G. Egloff. Desulfurizing cracked gasoline in the vapor phase with ozone and an electric discharge.
- U. S. 1,805,444, May 12, 1931. H. H. Wilson. Low-boiling petroleum distil-

- lates are freed from elemental sulfur, hydrogen sulfide, and mercaptans by treating in the liquid phase with anhydrous potassium hydroxide.
- U. S. 1,805,686, May 19, 1931. R. Cross. Desulfurizing cracked gasoline in the vapor phase by treating with molten sodium metal.
- U. S. 1,807,924, June 2, 1931. P. L. Magill. Treating crude gasoline in a rectifier with alkali metals to remove sulfur.
- U. S. 1,809,554, June 9, 1931. J. H. Hirt. Desulfurization and sweetening of gasoline by a composition made from caustic alkali, litharge, and caustic lime.
- U. S. 1,810,369, June 16, 1931. A. G. Peterkin, Jr. Sweetening of light distillates with oxygen in the presence of catalysts, such as cupric chloride, lead sulfide, or other lead compounds, suspended in sodium hydroxide solution.
- U. S. 1,810,803, June 16, 1931. H. Ulrich. Desulfurization of light petroleum distillates from Mexican, Texas, or California crudes by contacting the dry oil at about 0° F. with ozonized air and filtering out the solid material.
- U. S. 1,814,410, July 14, 1931. A. Richter and W. Schäfer. Purifying hydrocarbon oils in the vapor phase with ferric oxide and then in the liquid phase with activated carbon and hydrochloric acid.
- U. S. 1,815,563, July 21, 1931. L. M. Henderson and H. C. Cowles, Jr. Sweetening petroleum distillates with cupric chloride in the presence of sodium borate or sodium phosphate, and regenerating the solution with a current of air.
- U. S. 1,825,861, Oct. 6, 1931. T. T. Gray. Sweetening cracked gasolines by distilling them in contact with copper acetate or lead acetate and passing the vapors through fuller's earth.
- U. S. 1,828,734, Oct. 27, 1931. J. L. Dormon. Desulfurization of gasoline with nickel or similar metals.
- U. S. 1,831,916, Nov. 17, 1931. T. B. Kimball. Sweetening gasoline in the vapor phase with sodium hydroxide solution of 11-12.5% strength.
- U. S. 1,832,461, Nov. 17, 1931. A. Holmes and L. Burgess. Revivifying spent doctor solution by heating with sodium carbonate in the presence of oxygen.
- U. S. 1,840,269, Jan. 5, 1932. P. Borgstrom. A distillate containing mercaptans is sweetened by mixing it with another distillate containing organic peroxides.
- U. S. 1,843,578, Feb. 2, 1932. H. H. Meier and O. H. Dawson. Regenerating sodium plumbite by separating lead sulfide and agitating the lead sulfide with sulfur dioxide solution and then with sodium hydroxide solution.
- U. S. 1,845,723, Feb. 16, 1932. G. C. Rowden. Sweetening petroleum oils with sulfuric acid, clay, sodium hydroxide, and sodium hypochlorite.
- U. S. 1,855,486, Apr. 26, 1932. J. C. Morrell and G. Egloff. Cracked distillates are treated with sulfur dioxide and oxygen-containing gases in the presence of ferric sulfate.
- U. S. 1,858,635, May 17, 1932. A. R. Martin, P. J. Kelly, and K. H. Repath. Gasolines are sweetened by treatment with sodium plumbite solution. The partially exhausted solution is separated, and substantially anhydrous lead sulfide is precipitated from the oil, converted into lead sulfate and then dissolved in the partially exhausted alkali solution to convert it into an active reagent.
- U. S. 1,859,027, May 17, 1932. R. Cross. Cracked distillates are treated with molten metallic sodium intermingled with a non-reactive hydrocarbon gas.
- U. S. 1,862,003, June 7, 1932. P. J. Carlisle and C. R. Harris. Hydrocarbon oils are treated by passing them through metallic sodium suspended in liquid hydrocarbon material.
- U. S. 1,862,952, June 14, 1932. W. F. Bleeker. Oils are desulfurized by chlorine produced by electrolysis of brine in the presence of the oil. The gas is then displaced with hydrogen which is also produced electrolytically in the presence of petroleum.
- U. S. 1,863,967, June 21, 1932. G. H. Burruss. Petroleum distillates are sweetened with a mixture of lead oxide and lead sulfide in sodium hydroxide solution oxidized with air. Sulfur is added to the oil.
- U. S. 1,864,687, June 28, 1932. J. D. Fields. Cracked distillates produced by heating petroleum with a small propor-

- tion of sawdust or similar material are treated in the liquid phase with metallic sodium at atmospheric temperature.
- U. S. 1,864,719, June 28, 1932. J. D. Fields. Petroleum distillates are refined with metallic sodium, potassium, or lithium at ordinary temperatures.
- U. S. 1,865,797, July 5, 1932. W. H. Shiffler. Aluminum chloride sludge is atomized with steam at above 212° F. to produce hydrochloric acid.
- U. S. 1,867,697, July 19, 1932. F. G. Graves. Gum-forming constituents are removed from petroleum distillates by heating the oil with metallic copper, and treating the oil with clay.
- U. S. 1,869,781, Aug. 2, 1932. W. H. Shiffler, M. M. Holm, and M. F. Miller. Petroleum distillates cracked by an aluminum chloride catalyst are dechlorinated by heating to above 300° F.
- U. S. 1,872,446, Aug. 16, 1932. R. A. Halloran, M. L. Chappell, and J. H. Osmer. Hydrocarbon oils are purified by contacting them with aluminum chloride in the vapor phase.
- U. S. 1,875,088, Aug. 30, 1932. P. W. Merchant. Lead plumbite solution is revived by distilling out the oil and water, and oxidizing the residue with air.
- U. S. 1,882,000, Oct. 11, 1932. R. Cross. Cracked gasoline vapors are treated with iron oxide and with a mixture of fuller's earth and copper oxide.
- U. S. 1,882,146, Oct. 11, 1932. H. N. Holmes. Petroleum distillates are desulfurized by treating them with an iron-silica gel containing copper sulfide.
- U. S. 1,883,947, Oct. 25, 1932. A. Kinsel. Spent sodium plumbite solution is heated and agitated, followed by settling, for recovering lead. Apparatus is described.
- U. S. 1,888,219, Nov. 22, 1932. H. H. Cannon. Gasoline is sweetened with a reagent comprising lead oxide, calcium hydroxide, and an adsorbent earth suspended in sodium hydroxide solution.
- U. S. 1,888,382, Nov. 22, 1932. F. W. Heath. Gasoline is sweetened and its color stabilized by contacting with a solution of potassium ferricyanide, followed by refining with sulfuric acid and neutralizing.
- U. S. 1,889,388, Nov. 29, 1932. M. Smith. Gasoline is desulfurized by passing its vapors mixed with hydrogen over cadmium or copper chromite.
- U. S. 1,890,516, Dec. 13, 1932. A. Lachman. Gasoline is sweetened and made non-corrosive by treating with a solution of sodium hydroxide having a pH greater than 7.4 and containing activated charcoal and air.
- U. S. 1,890,881, Dec. 13, 1932. P. L. Magill. Petroleum distillates are desulfurized by passing their vapors over a finely divided alkali metal dispersed in a semi-solid mass.
- U. S. 1,891,619, Dec. 20, 1932. M. L. Chappell. Motor fuels are prepared by heating distillates with chlorine at not above 100° F., followed by refining with aluminum chloride at 150-350° F. and under pressure.
- U. S. 1,892,801, Jan. 3, 1933. F. E. Kimball. Refining light distillates by contacting their vapors with a hot mixture of calcium and magnesium chlorides followed by fractionation.
- U. S. 1,895,223, Jan. 24, 1933. F. E. Kimball. Gasoline is refined in the vapor phase with a water solution of berillium chloride and ammonium chloride.
- U. S. 1,897,617, Feb. 14, 1933. L. A. Mекler. Gasoline is sweetened by X-ray treatment.
- U. S. 1,899,042, Feb. 28, 1933. W. M. Malisoff. Oils are desulfurized by washing with a solution of alkali sulfide in methyl, ethyl, propyl, or isopropyl alcohol, glycol, glycerol, acetone, methyl ethyl ketone, di-ethyl ketone, or their mixtures.
- U. S. 1,899,314, Feb. 28, 1933. T. W. Culmer. Light petroleum distillates are desulfurized by treatment with cadmium-ammonium chloride or nitrate.
- U. S. 1,904,172, Apr. 18, 1933. H. Rostin. Materials such as gas oil are desulfurized by passing them at elevated temperatures over minette freshly reduced with hydrogen.
- U. S. 1,904,173, Apr. 18, 1933. R. K. Stratford and W. P. Doohan. Corrosive sulfur is removed from petroleum distillates by contacting them at 100-150° F. with an alkaline solution containing rosin.
- U. S. 1,904,382, Apr. 18, 1933. J. C. Morrell. Gasolines are sweetened with

- sodium plumbite solution, and the mercaptides are precipitated by exposing the material to ultra-violet light.
- U. S. 1,908,273, May 9, 1933. M. C. Taylor. Sweetening gasoline with a solution of chlorous and hydrochloric acids.
- U. S. 1,910,288, May 23, 1933. J. H. Hirt. Gasoline is sweetened by treating with a dry mixture of sodium hydroxide, lead oxide, and lime.
- U. S. 1,911,640, May 30, 1933. J. C. Morrell. Sweetening of light petroleum distillates by filtering them through a solid adsorbent containing copper salt and an alkali metal hydroxide.
- U. S. 1,914,953, June 20, 1933. B. Malishev. Refining light distillates by heating with phosphorus pentoxide to produce a sweetened, non-corrosive, gum-free, and antiknock product.
- U. S. 1,920,247, Aug. 1, 1933. R. B. Day. Gum-free and non-corrosive products are obtained by treating cracked distillates with hydrochloric acid in the presence of a free metal, such as aluminum, manganese, zinc, chromium, iron, cadmium, cobalt, nickel, tin, lead, antimony, bismuth, arsenic, copper, or mercury.
- U. S. 1,920,270, Aug. 1, 1933. J. C. Morrell. Light petroleum distillates are treated at elevated temperature but in the liquid phase with hydrochloric acid in the presence of zinc, tin, or iron.
- U. S. 1,924,911, Aug. 29, 1933. H. H. Cannon. Acid-treated gasoline is sweetened by mixing with finely divided sodium hydroxide and sulfur and then contacting with a dry powdered mass containing sodium hydroxide and lead oxide.
- U. S. 1,926,226, Sept. 12, 1933. H. H. Cannon. Gasoline containing mercaptans and free sulfur is sweetened by passing through a mixture of lead oxide, sodium hydroxide, lime, and adsorbent material.
- U. S. 1,926,515, Sept. 12, 1933. B. F. Dooley, Jr. Sludge from sodium plumbite treatment is exposed to the air to render lead compounds soluble in sodium hydroxide solutions.
- U. S. 1,927,068, Sept. 19, 1933. R. S. McClaughry and L. V. Moore. Gasoline is sweetened by contacting with sodium plumbite solution in the absence of free sulfur, washing with water, and treating with an alkaline hypochlorite solution.
- U. S. 1,927,147, Sept. 19, 1933. F. B. Behrens. Oils are sweetened by treating with sodium plumbite solution and then with a permanganate.
- U. S. 1,927,182, Sept. 19, 1933. J. C. Morrell. Gasoline is sweetened by converting mercaptans into mercaptides with suitable reagents and then converting them to disulfides with sodium perborate.
- U. S. 1,930,216, Oct. 10, 1933. H. C. Weber. Gasoline is desulfurized with a mixture of sodium carbonate and sodium chloride in the presence of metallic silver and metals, such as aluminum.
- U. S. 1,932,174, Oct. 24, 1933. W. Gaus and M. Pier. Petroleum is desulfurized by treatment with hydrogen in the presence of catalysts.
- U. S. 1,932,186, Oct. 24, 1933. M. Pier, F. Ringer, and W. Simon. Desulfurizing petroleum distillates by treatment with hydrogen in the presence of catalysts.
- U. S. 1,934,068, Nov. 7, 1933. E. M. Jolly and C. C. Swoope. Traces of chlorine are removed from oils obtained by aluminum chloride refining by treatment with metallic sodium.
- U. S. 1,935,725, Nov. 21, 1933. R. Schuhmann. Petroleum oils are freed from elemental sulfur by washing with a sodium hydroxide solution, dehydrating with an adsorbent, and further treatment with an alcoholic potassium hydroxide solution.
- U. S. 1,936,629, Nov. 28, 1933. P. L. Krauel and G. W. Watts. Cracked distillate is treated with sodium plumbite solution, heated to decompose the lead compounds, and partially distilled. Lead sulfide is separated from the unvaporized fraction.
- U. S. 1,937,873, Dec. 5, 1933. R. B. Day. Color compounds, gum-forming substances, and sulfur compounds are removed by heating cracked gasoline with hydrochloric acid in contact with brass or other metallic material.
- U. S. 1,937,914, Dec. 5, 1933. H. Pines. Cracked distillates are desulfurized in the vapor phase with sodamide.

- U. S. 1,938,116, Dec. 5, 1933. W. A. Smith. Petroleum distillates are deodorized with metallic cadmium.
- U. S. 1,938,117, Dec. 5, 1933. W. A. Smith. Desulfurizing gasoline with a mixture of copper and zinc silicates. Copper nitrate and similar compounds may also be used.
- U. S. 1,938,670, Dec. 12, 1933. F. W. Sullivan, Jr., and A. B. Brown. Petroleum oils are desulfurized by contacting with colloidal metallic sodium.
- U. S. 1,938,671, Dec. 12, 1933. F. W. Sullivan, Jr., and A. B. Brown. Petroleum oils are desulfurized with metallic sodium.
- U. S. 1,938,672, Dec. 12, 1933. R. F. Ruthruff. Light petroleum distillates are desulfurized by agitation with molten sodium.
- U. S. 1,939,839, Dec. 19, 1933. E. C. Williams and H. P. A. Groll. Cracked distillates are sweetened by contacting with amalgams of sodium or potassium.
- U. S. 1,940,726, Dec. 26, 1933. J. C. Morrell. Cracked distillates are desulfurized with an alcoholic solution of an alkali or alkali earth sulfide.
- U. S. 1,940,861, Dec. 26, 1933. L. M. Henderson. Sweetening petroleum distillates with sodium plumbite solution, followed by washing with copper chloride solution.
- U. S. 1,943,744, Jan. 16, 1934. L. Rosenstein. Mercaptans are removed from hydrocarbon oils by treating with sodium carbonate or bicarbonate solution and then with a strong alkaline solution. The solution is regenerated by oxidation with air in the presence of catalysts, such as nickel or cobalt sulfide.
- U. S. 1,944,170, Jan. 23, 1934. H. T. Darlington. Oils are desulfurized with colloidal iron.
- U. S. 1,945,121, Jan. 30, 1934. W. L. Savell. Oils are sweetened with calcium hypochlorite solution.
- U. S. 1,948,528, Feb. 27, 1934. W. M. Malisoff. Cracked gasoline is desulfurized by treatment with aluminum chloride.
- U. S. 1,948,565, Feb. 27, 1934. R. B. Day. Cracked gasolines are sweetened with a mixture of copper sulfate or copper oxide and ammonium chloride, and then filtered through fuller's earth.
- U. S. 1,949,756, Mar. 6, 1934. J. C. Morrell. Hydrocarbon oils are sweetened by treatment with sodium plumbite solution, and then contacted with a soluble sulfide and fuller's earth.
- U. S. 1,950,735, Mar. 13, 1934. I. Levine. Hydrocarbon distillates are desulfurized by treating with acetone in the presence of zinc or aluminum chloride.
- U. S. 1,951,324, Mar. 13, 1934. E. A. Bosing. Cracked distillates are sweetened by treatment with sodium plumbite solution and then contacting with a hydrogen peroxide solution.
- U. S. 1,952,616, Mar. 27, 1934. R. Vose. Lubricating oils are refined by agitating with molten sodium.
- U. S. 1,952,751, Mar. 27, 1934. T. T. Gray. Cracked distillates are refined in the vapor phase with copper oxide deposited on fuller's earth.
- U. S. 1,954,486, Apr. 10, 1934. J. C. Morrell and G. Egloff. Cracked distillates are refined in the vapor phase with hydrogen chloride in the presence of zinc chloride solution and solid copper chloride.
- U. S. 1,954,487, Apr. 10, 1934. J. C. Morrell and G. Egloff. Cracked distillates are refined in the vapor phase with a solution of sodium pyrosulfate.
- U. S. 1,954,488, Apr. 10, 1934. J. C. Morrell and G. Egloff. Hydrocarbon oils are refined in the vapor phase with a solution of ammonium persulfate.
- U. S. 1,954,843, Apr. 17, 1934. R. E. Schaad. Oils are desulfurized by treating them, preferably in the vapor phase, with a nitride of copper, calcium, strontium, barium, magnesium, aluminum, thorium, manganese, iron, nickel, or cobalt.
- U. S. 1,954,867, Apr. 17, 1934. G. Egloff. Cracked distillates are treated in the vapor phase with zinc chloride in the presence of ultra-violet light.
- U. S. 1,955,607, Apr. 17, 1934. H. V. Rees and C. F. Teichmann. Petroleum distillates are sweetened with a mixture of fuller's earth, sodium hydroxide, sulfur, and sodium peroxide.
- U. S. 1,960,624, May 29, 1934. G. Egloff. Cracked distillates are desulfurized with hydrogen in the presence of carbonyl chloride and charcoal.

- U. S. 1,962,182, June 12, 1934. G. Egloff. Cracked distillates are refined with steam in the presence of sodium.
- U. S. 1,962,698, June 12, 1934. R. S. Vose. Refining hydrocarbon oils with metallic sodium.
- U. S. 1,963,556, June 19, 1934. J. C. Morrell. Cracked distillates are treated with a solution of mercuric chloride and cupric chloride.
- U. S. 1,964,087, June 26, 1934. W. A. Smith. Cracked distillates are purified with dry copper silicate.
- U. S. 1,964,219, June 26, 1934. W. A. Schulze and F. E. Frey. Gasoline is sweetened with a solution of cupric sulfate and sodium chloride.
- U. S. 1,964,220, June 26, 1934. W. A. Schulze and F. E. Frey. Gasoline is sweetened with a solution of cupric sulfate and sodium bromide.
- U. S. 1,965,821, July 10, 1934. H. T. Bennett. Sweetening cracked distillates by percolating them through brucite and then contacting with clay impregnated with cupric chloride.
- U. S. 1,967,173, July 17, 1934. J. C. Morrell and G. Egloff. Cracked distillates are refined in the vapor phase with a solution of hypochlorous, chloric, bromic, or iodic acid containing copper or iron.
- U. S. 1,967,174, July 17, 1934. J. C. Morrell and G. Egloff. Cracked distillates are refined in the vapor phase with a solution of oxygenated halogen acid containing zinc chloride.
- U. S. 1,968,089, July 31, 1934. J. C. Morrell. Cracked distillates are sweetened with a mixture of sodium silicate and litharge containing silicic acid.
- U. S. 1,968,842, Aug. 7, 1934. W. M. Malisoff. Sweetening cracked petroleum distillates with a solution of sodium hydroxide in methyl alcohol containing sufficient water to render the solution insoluble in the oil.
- U. S. 1,968,843, Aug. 7, 1934. W. M. Malisoff. Sludges from treating petroleum oils with sodium hydroxide solution in methyl alcohol are heated to volatilize the solvent and treated with steam to effect hydrolysis.
- U. S. 1,969,302, Aug. 7, 1934. G. Egloff and J. C. Morrell. Refining cracked distillates in the vapor phase with phosphoric acid and cobalt chromate deposited on fuller's earth. Permanganates or hypochlorites may also be used.
- U. S. 1,970,281, Aug. 14, 1934. R. B. Day. Cracked gasoline vapors are refined with hydrogen chloride and then with ammonia in the presence of zinc, cadmium, mercury, lead, or copper.
- U. S. 1,970,282, Aug. 14, 1934. R. B. Day. Cracked gasoline vapors are refined with hydrogen chloride in the presence of an ore of zinc, copper, or lead.
- U. S. 1,970,283, Aug. 14, 1934. R. B. Day. Cracked gasoline is refined at an elevated temperature with hydrogen chloride in the presence of zinc ore, such as zinc silicate or carbonate.
- U. S. 1,970,693, Aug. 21, 1934. H. G. M. Fischer. Separation of oil and lead sulfide from spent sodium plumbite solutions by centrifuging.
- U. S. 1,971,167, Aug. 21, 1934. M. C. Sumpter. Cracked distillates are purified with a molten mixture of aluminum chloride and another metallic chloride, such as potassium, ammonium, cuprous, barium, magnesium, lithium, sodium, or stannous chloride.
- U. S. 1,972,102, Sept. 4, 1934. W. M. Malisoff. Desulfurizing light petroleum oils with acetic acid and hydrogen peroxide.
- U. S. 1,973,499, Sept. 11, 1934. J. C. Morrell. Cracked distillates are desulfurized by heating with ferric chloride, followed by treatment with molten sodium or sodamide.
- U. S. 1,973,500, Sept. 11, 1934. J. C. Morrell. Cracked distillates are refined in the vapor phase with air in the presence of a mixture of lime, ferric oxide, and fuller's earth, and then with sulfuric acid containing sodium acid sulfate.
- U. S. 1,973,895, Sept. 18, 1934. C. W. Garrison. Oils are desulfurized by contacting with a solution of sodium carbonate and arsenic trioxide.
- U. S. 1,974,311, Sept. 18, 1934. I. Levine. Cracked distillates are refined in the vapor phase with formaldehyde or acetaldehyde in the presence of hydrogen chloride and zinc or aluminum.
- U. S. 1,977,631, Oct. 23, 1934. E. C. Higgins, Jr., and F. T. Gardner. Sweet-

- ening gasoline by adding sulfur and passing the mixture through brucite.
- U. S. 1,977,993, Oct. 23, 1934. M. L. Kirk. Material from old storage batteries is treated with sodium carbonate; the mixture is roasted and treated with sodium hydroxide to produce the sodium plumbite solution.
- U. S. 1,979,448, Nov. 6, 1934. H. H. Cannon. Sweetening cracked distillates with a slurry of calcium hydroxide and lead oxide in a sweetened oil.
- U. S. 1,979,565, Nov. 6, 1934. J. C. Morrell and G. Egloff. Cracked gasoline is refined with sulfur dioxide and air in the vapor phase in the presence of zinc or tin oxide and steam.
- U. S. 1,980,189, Nov. 13, 1934. R. F. Davis. Partially desulfurized distillates are further desulfurized by treatment with chlorine, bromine, or iodine and piperidine.
- U. S. 1,980,555, Nov. 13, 1934. W. A. Schulze and F. E. Frey. Cracked distillates sweetened with copper salts are stabilized by treatment with sodium sulfide.
- U. S. 1,983,220, Dec. 4, 1934. J. D. Fields. Cracked distillates are treated with sodium, potassium, or lithium and then with a solution of magnesium, ferric, zinc, or aluminum chloride.
- U. S. 1,985,955, Jan. 1, 1935. L. J. Snyder. Cracked distillates are sweetened with sodium plumbite solution in the presence of sulfur insufficient to cause precipitation of lead sulfide.
- U. S. 1,986,565, Jan. 1, 1935. E. F. Engelke. Sweetening cracked distillates by contacting them with sodium plumbite solution containing sulfur and fractionally distilling in the presence of a cracked hydrocarbon gas free of sulfur.
- U. S. 1,988,083, Jan. 15, 1935. J. C. Morrell. Cracked distillates are treated in the vapor phase with a solution of ferric chloride containing hydrochloric acid.
- U. S. 1,988,114, Jan. 15, 1935. G. Egloff and J. C. Morrell. Cracked distillates are treated in the vapor phase with a solution of cupric chloride in the presence of hydrochloric acid.
- U. S. 1,993,140, Mar. 5, 1935. W. G. Hamilton, R. G. Follis, and H. P. McCormick. Oil containing hydrogen sulfide is agitated with a sulfur dioxide solution, and the resulting product containing elemental sulfur is used in treating oils with sodium plumbite solution.
- U. S. 1,994,969, Mar. 19, 1935. R. B. Thacker, Jr. Sweetening cracked distillates with sodium plumbite solution and elemental sulfur, and heating the treated gasoline to remove the sulfur and lead compounds.
- U. S. 1,996,236, Apr. 2, 1935. A. F. Endres. Sweetening cracked distillates with sodium plumbite solution.
- U. S. 1,997,861, Apr. 16, 1935. G. Egloff and J. C. Morrell. Cracked gasoline vapors are passed through hypochlorous acid solution containing a dissolved salt of copper.
- U. S. 1,998,849, Apr. 23, 1935. W. A. Schulze. Mercaptans are removed by washing with sodium hydroxide solution.
- U. S. 1,998,863, Apr. 23, 1935. L. V. Chaney and W. A. Schulze. Mercaptans are removed from cracked distillates by washing with sodium hydroxide solution, which solution is regenerated by blowing with air.
- U. S. 1,999,041, Apr. 23, 1935. A. E. Dunstan. Gasoline is deodorized by contacting with a reagent capable of liberating chlorine.
- U. S. 2,001,185, May 14, 1935. R. B. Day. Hydrocarbon vapors are refined with hydrogen chloride and steam, and the resulting mixture is contacted with a solution of zinc chloride which contains copper chloride.
- U. S. 2,001,634, May 14, 1935. D. R. Stevens and W. A. Gruse. Petroleum distillates are treated with aluminum chloride in the presence of phenol.
- U. S. 2,002,747, May 28, 1935. J. C. Morrell. Cracked distillates are refined by mixing their vapors with ammonia and passing them through molten sodium or calcium.
- U. S. 2,009,879, July 30, 1935. G. Egloff. Treating cracked gasoline vapors with hydrogen in the presence of zinc chloride solution.
- U. S. 2,009,898, July 30, 1935. J. C. Morrell. Cracked distillates are treated in the vapor phase with nitrogen dioxide.

- U. S. 2,009,954, July 30, 1935. R. E. Burk. Sweetening gasoline with sodium hydroxide solution and sulfur.
- U. S. 2,011,954, Aug. 20, 1935. C. F. Teichmann. Sweetening cracked distillates with a suspension of lead sulfide in sodium hydroxide solution containing sodium peroxide.
- U. S. 2,013,293, Sept. 3, 1935. W. N. Davis and M. M. Holm. Cracked gasoline vapors are contacted with sodium plumbite solution to remove mercaptans, and the resulting mercaptides are hydrolyzed with steam.
- U. S. 2,013,400, Sept. 3, 1935. W. L. Benedict and C. Wirth, III. Cracked distillates are treated with hydrochloric acid containing dissolved ferric sulfate.
- U. S. 2,015,038, Sept. 17, 1935. E. F. Pevere. Cracked distillates are sweetened with a solution of phenol or aminophenol containing hydrogen peroxide or sodium peroxide.
- U. S. 2,015,080, Sept. 24, 1935. W. M. Malisoff. Oils are desulfurized by contacting their vapors with aluminum sulfide.
- U. S. 2,016,272, Oct. 8, 1935. A. E. Buell and W. A. Schulze. Cracked distillates are sweetened by contacting their vapors with chromite ore, vanadinite, or descloizite.
- U. S. 2,016,342, Oct. 8, 1935. P. S. Nisson. Cracked distillates are sweetened with sodium plumbite solution in the presence of sulfur, and then by treating with sodium or calcium hypochlorite solutions.
- U. S. 2,019,772, Nov. 5, 1935. A. J. van Peski. Treating gasolines with aluminum chloride in the presence of nitromethane.
- U. S. 2,020,661, Nov. 12, 1935. W. A. Schulze and L. V. Chaney. Elemental sulfur is removed from petroleum oils by contacting them with a solution of polysulfides of alkali or alkali-earth metals.
- U. S. 2,021,739, Nov. 19, 1935. J. C. Morrell and G. Egloff. Vapor-phase refining of gasolines with hypochlorous acid in the presence of zinc chloride.
- U. S. 2,021,740, Nov. 19, 1935. J. C. Morrell and G. Egloff. Vapor-phase refining of gasolines with solutions of hypochlorous, chloric, or iodic acids.
- U. S. 2,022,550, Nov. 26, 1935. F. W. Stone and J. N. Garrison. Regenerating spent sodium plumbite solution by air agitation.
- U. S. 2,022,558, Nov. 26, 1935. B. F. Dooley, Jr. Lead sludge from sodium plumbite treatment is washed with naphtha before dissolving it in sodium hydroxide solution.
- U. S. 2,022,847, Dec. 3, 1935. A. F. Endres. Light petroleum distillates are sweetened with plumbite solution prior to adding gum inhibitors.
- U. S. 2,022,942, Dec. 3, 1935. W. A. Schulze and L. V. Chaney. Oils containing sulfur compounds having oxidizing properties and formed in sweetening with hypochlorites are treated with mercaptans to convert them into disulfides.
- U. S. 2,024,968, Dec. 17, 1935. J. D. Fields. Desulfurizing oils by heating in closed containers with wood, cane refuse, or similar materials, followed by distillation.
- U. S. 2,025,255, Dec. 24, 1935. J. F. M. Taylor and H. I. Lounsbury. Fractionation of gasoline to separate into fractions rich and poor in sulfur compounds.
- U. S. 2,026,492, Dec. 31, 1935. H. T. Bennett, H. H. Hopkins, and J. R. Marshall. Refining petrolatum with a mixture of uranium nitrate and anhydrous aluminum chloride.
- U. S. 2,027,770, Jan. 14, 1936. J. D. Fields. Refining lubricating oils with metallic sodium.
- U. S. 2,028,998, Jan. 28, 1936. W. A. Schulze and L. V. Chaney. Refining cracked distillates with a hypochlorite solution, followed by treatment with a sulfite, cyanide, or stannite of alkali or alkali-earth metals.
- U. S. 2,029,100, Jan. 28, 1936. A. V. Grosse. Desulfurizing cracked distillates with hydrogen in the presence of a cobalt thio-molybdate or thio-tungstate.
- U. S. 2,031,972, Feb. 25, 1936. F. R. Moser. Gasoline is sweetened with sodium hydroxide solution and elemental sulfur, and tetrahydronaphthalene or pinene or cyclohexene is added to the product to inhibit the corrosive action of elemental sulfur.

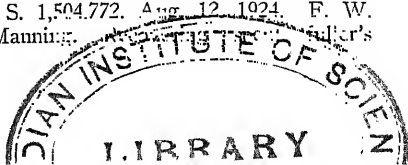
- U. S. 2,032,896, Mar. 3, 1936. C. L. Smith and W. G. Annable. Desulfurizing oils with copper oxide.
- U. S. 2,034,068, Mar. 17, 1936. J. F. Wait. Refining heavy petroleum distillates in the vapor phase with metallic sodium.
- U. S. 2,034,837, Mar. 24, 1936. W. A. Schulze and L. V. Chancy. Sweetening cracked distillates with a solution of sodium hydroxide and sodium polysulfide.
- U. S. 2,035,609, Mar. 31, 1936. A. Lachman. Refining gasoline with a solution of copper chloride at elevated temperature and pressure.
- U. S. 2,036,396, Apr. 7, 1936. L. P. Chebotar. Refining light distillates with air in the presence of oxidation promoters, such as pyridine or hydroquinone, and oil-soluble soaps of manganese, copper, cobalt, nickel, or lead.
- U. S. 2,037,781, Apr. 21, 1936. A. V. Grosse. Desulfurization of oil distillates by hydrogenation in the presence of cobalt thiomolybdate-sodium aluminate catalyst.
- U. S. 2,037,789-92, Apr. 21, 1936. V. Ipatieff. Desulfurization of oils with hydrogen.
- U. S. 2,040,366, May 12, 1936. G. Egloff and J. C. Morrell. Cracked distillates are purified in the vapor phase with sulfur dioxide and steam in the presence of zinc sulfate.
- U. S. 2,041,364, May 19, 1936. W. Miller. Desulfurization of cracked distillates with absorbents, followed by fractionation.
- U. S. 2,042,050, May 26, 1936. C. O. Hoover. Sweetening gasolines by passing them through an adsorbent impregnated with cupric chloride, and regenerating the reagent with oxygen or air.
- U. S. 2,042,051, May 26, 1936. C. O. Hoover. Sweetening gasoline with oxygen in the presence of cupric chloride deposited on an adsorbent.
- U. S. 2,042,052, May 26, 1936. C. O. Hoover. Sweetening gasoline with oxygen in the presence of cupric chloride and mercurous chloride deposited on an adsorbent.
- U. S. 2,042,053, May 26, 1936. C. O. Hoover. Sweetening gasoline by contacting with cupric chloride, followed by treatment with oxygen in the presence of an adsorbent.
- U. S. 2,042,054, May 26, 1936. C. O. Hoover. Sweetening hydrocarbon oils with cupric chloride and potassium permanganate deposited on an adsorbent.
- U. S. 2,042,055, May 26, 1936. C. O. Hoover. Sweetening gasoline with sodium plumbite solution in the presence of oxygen.
- U. S. 2,042,056, May 26, 1936. O. Codier. Sweetening gasoline with sodium plumbite solution, followed by contacting with adsorbents. Adsorbents are then extracted with sodium hydroxide solution for the recovery of lead.
- U. S. 2,042,298, May 26, 1936. G. H. B. Davis. Purification and desulfurization of light distillates with hydrogen.
- U. S. 2,042,557, June 2, 1936. W. J. Sparks. Lubricating oils are refined with oxygen in the presence of sodium metal.
- U. S. 2,042,718, June 2, 1936. A. Lachman. Refining cracked distillates in the vapor phase with a solution of zinc chloride containing oxide and hydroxide of zinc.
- U. S. 2,045,057, June 23, 1936. W. A. Schulze. Naphthas containing carbon disulfide are refined with morpholine.
- U. S. 2,045,262, June 23, 1936. S. Comay. Cracked distillates are desulfurized by heating with ferric nitrate and then treating with sodium hydroxide solution and sulfuric acid.
- U. S. 2,048,169, July 21, 1936. N. D. Scott. Refining cracked distillates with an addition compound of sodium and naphthalene, anthracene, or biphenyl in the presence of ether.
- U. S. 2,048,241, July 21, 1936. M. P. Youker. Separation of hydrogen sulfide from gasoline by fractionation.
- U. S. 2,050,772, Aug. 11, 1936. J. F. Wait. Treating oils with an oxidizing agent, followed by vapor phase refining with molten sodium.
- U. S. 2,051,939, Aug. 25, 1936. R. B. Day. Refining cracked distillates with hydrogen chloride in the presence of cupric chloride.
- U. S. 2,052,239, Aug. 25, 1936. R. W. Miller. Preparation of sodium plumbite solution from lead oxide and impure rayon waste.

- U. S. 2,053,909, Sept. 8, 1936. H. L. Kerr. Sodium ortho-plumbate is used for refining light petroleum distillates, preferably in admixture with sodium plumbite.
- U. S. 2,055,027, Sept. 22, 1936. R. B. Day. Refining light distillates with hydrogen chloride in the presence of zinc chloride at elevated temperatures and under pressure.
- U. S. 2,055,423, Sept. 22, 1936. A. Belchetz. Gasoline is sweetened by dividing it into two portions, treating one portion with sodium plumbite solution, and blending it with the untreated portion in the presence of sulfur.
- U. S. 2,056,618, Oct. 6, 1936. W. V. Overbaugh. Gasoline is sweetened by mixing with a sweetened product, adding sulfur, and agitating the mixture with sodium plumbite solution or with a lead sulfide suspension in sodium hydroxide solution.
- U. S. 2,057,424, Oct. 13, 1936. G. Egloff and J. C. Morrell. Cracked distillates are refined in the vapor phase with hydrogen chloride in the presence of mercuric chloride solution.
- U. S. 2,057,629, Oct. 13, 1936. J. C. Morrell and G. Egloff. Cracked distillates are refined in the liquid phase with zinc or tin oxide in the presence of hydrogen chloride.
- U. S. 2,057,630, Oct. 13, 1936. J. C. Morrell and G. Egloff. Cracked distillates are refined in the vapor phase with zinc or tin oxide in the presence of hydrogen chloride.
- U. S. 2,057,918, Oct. 20, 1936. C. M. Ridgway. Gasoline is sweetened by washing with sodium plumbite solution and settling for several days.
- U. S. 2,058,131, Oct. 20, 1936. P. J. Carlisle. Lubricating oils are treated with molten sodium, followed by refining with fuller's earth.
- U. S. 2,058,534, Oct. 27, 1936. J. F. Wait. Lubricating oils are refined by extraction with liquid sulfur dioxide, followed by contacting with molten sodium.
- U. S. 2,058,720, Oct. 27, 1936. J. A. Reid and W. A. Schulze. Gasoline is sweetened with a cupric chloride or bromide solution.
- U. S. 2,058,958, Oct. 27, 1936. R. B. Day. Hydrocarbon distillates are refined by passing their vapors mixed with hydrogen chloride through a suspension of oxides of zinc, aluminum, iron, chromium, magnesium, cobalt, nickel, calcium, sodium, potassium, lead, or tin into a high-boiling hydrocarbon oil.
- U. S. 2,059,075, Oct. 27, 1936. D. I. Yabroff and J. W. Givens. Sweetening gasoline by extraction with sodium hydroxide or trimethyl ammonium hydroxide solutions.
- U. S. 2,059,542, Nov. 3, 1936. J. F. Wait. Refining petroleum oils in the vapor phase with a mixture of sodium hydroxide and metallic sodium.
- U. S. 2,060,112, Nov. 10, 1936. R. B. Pierce and A. W. Trusty. Desulfurizing cracked distillates by passing their vapors over steel wool impregnated with cadmium sulfide.
- U. S. 2,061,583, Nov. 24, 1936. W. M. Malisoff and F. G. Hess. Gasoline is refined with phosphoric acid and phenol, cresol, or naphthol at 150-300° C.
- U. S. 2,061,845, Nov. 24, 1936. J. C. Morrell. Cracked distillates are desulfurized by hydrogenation.
- U. S. 2,063,082, Dec. 8, 1936. R. B. Day. Cracked distillates are refined at elevated temperatures with hydrogen chloride in the presence of chlorides of zinc or copper.
- U. S. 2,063,491, Dec. 8, 1936. R. B. Day. Cracked distillates are treated with hydrochloric acid in the presence of zinc or mercuric chloride.
- U. S. 2,063,494, Dec. 8, 1936. G. Egloff and J. C. Morrell. Cracked distillates are treated in the vapor phase with hydrogen chloride and a solution of mercuric chloride in the presence of zinc oxychloride.
- U. S. 2,063,517, Dec. 8, 1936. J. C. Morrell and G. Egloff. Cracked distillates are treated at elevated temperatures with hydrochloric acid and cupric chloride.
- U. S. 2,063,860, Dec. 8, 1936. J. F. Wait. Refining lubricating oils with molten sodium.
- U. S. 2,064,558, Dec. 15, 1936. A. A. Morton. Refining cracked distillates with molten sodium and para-chlorotoluene.

- U. S. 2,073,147, Mar. 9, 1937. F. Gardner. Sweetening of petroleum distillates with sodium plumbite solution.
- U. S. 2,073,578, Mar. 9, 1937. M. H. Gwynn. Refining of petroleum distillates with hydrogen in the presence of copper, nickel, or cobalt catalysts.
- U. S. 2,073,973, Mar. 16, 1937. A. M. Muckenfuss. Lubricating oils are refined with hydrogen in the presence of sodium hydrocarbide.
- U. S. 2,075,151, Mar. 30, 1937. J. F. Wait. Refining lubricating oils with molten sodium.
- U. S. 2,078,468, Apr. 27, 1937. W. M. Stratford. Refining cracked distillates by heating with metallic sodium.
- U. S. 2,078,773, Apr. 27, 1937. E. T. Pummill. Regeneration of spent sodium plumbite solution with calcium or magnesium hydroxide, followed by oxidizing with air at elevated temperatures.
- U. S. 2,080,087, May 11, 1937. M. Mizuta and T. Yoshimura. Sweetening cracked distillates with heavy metallic soaps of abietic acid.
- U. S. 2,080,365, May 11, 1937. G. H. von Fuchs and L. E. Border. Sweetening of cracked distillates with copper turnings in the presence of ammonia.
- U. S. 2,080,654, May 18, 1937. W. A. Craig. Revivification of spent sodium plumbite solution with air.
- U. S. 2,084,575, June 22, 1937. C. A. Day, Jr. Removing mercaptans by washing gasoline with sodium hydroxide solution in alcohol and water.
- U. S. 2,085,523, June 29, 1937. A. Belchetz and B. R. Carney. Sweetening gasolines with a mixture of calcium hydroxide and ferrous sulfate in the presence of sulfur.
- U. S. 2,089,373, Aug. 10, 1937. R. W. Henry, J. A. Reid, and W. A. Schulze. Apparatus for sweetening gasoline with copper sulfate-sodium chloride solution.
- U. S. 2,090,190, Aug. 17, 1937. C. E. Dolbear. Sweetening of petroleum distillates with sodium ferrite.
- U. S. 2,091,239, Aug. 24, 1937. F. W. Hall. Naphtha is rendered non-corrosive by heating with copper naphthenate.
- U. S. 2,094,485, Sept. 28, 1937. A. E. Buell. Sweetening gasolines by contacting them in the presence of oxygen with fuller's earth impregnated with cupric sulfate and sodium chloride solutions.
- U. S. 2,098,059, Nov. 2, 1927. J. C. Morrell. Refining cracked distillates in the vapor phase with copper turnings in the presence of hydrogen chloride and formaldehyde.
- U. S. 2,098,943, Nov. 16, 1937. A. E. Buell and W. A. Schulze. Desulfurizing cracked distillates by passing their vapors over zinc ore.
- U. S. 2,104,791, Jan. 11, 1938. W. A. Craig. Refining cracked distillates in the vapor phase with solutions of chlorides, bromides, sulfates, or nitrates of zinc, copper, cadmium, iron, chromium, manganese, aluminum, nickel, or cobalt.
- U. S. 2,105,464, Jan. 18, 1938. W. C. Ault and C. A. Hochwalt. Cracked distillates are treated in the vapor phase with ferric oxide and then refined with phosphoric acid.
- U. S. 2,108,438, Feb. 15, 1938. F. E. Kimball. Refining cracked distillate by passing their vapors through molten mixture of ammonium and zinc chlorides.
- U. S. 2,110,403, Mar. 8, 1938. L. Rosenstein. Potassium phosphate is used for removing hydrogen sulfide from hydrocarbon gases.
- U. S. 2,110,745, Mar. 8, 1938. A. Stewart. Lead plumbite solution for sweetening light distillates is prepared from lead oxide, potassium or sodium hydroxide, and mercuric chloride.
- U. S. 2,111,487, Mar. 15, 1938. L. V. Chaney and A. E. Buell. Cracked distillates are sweetened by filtering in the presence of oxygen through an adsorbent impregnated with copper chloride.
- U. S. 2,114,313-4-5, Apr. 19, 1938. W. A. Patrick, Jr. Refining hydrocarbon oils with sulfur chloride.
- U. S. 2,114,354, Apr. 19, 1938. E. T. Pummill. Regeneration of sodium plumbite solutions with chlorine.
- U. S. 2,114,852, Apr. 19, 1938. D. S. McKittrick. Distillation of cracked products in the presence of furfural, methyl cyanide, or ethylenediamine, fol-

- lowed by refining of the residual fraction which contains the major portion of sulfur compounds.
- U. S. 2,115,063, Apr. 26, 1938. J. E. Drapeau. Sodium plumbite solution containing metallic antimony is used in sweetening oils.
- U. S. 2,121,169, June 21, 1938. F. E. Kimball. Cracked distillates are refined in the vapor phase with a molten mixture of ammonium pentachlorodizincate and ammonium chloride.
- U. S. 2,125,636, Aug. 2, 1938. W. W. Holland. Cracked distillate is sweetened with sodium plumbite solution, washed with acetic acid, and inhibited with triethylamine or catechol to prevent gum formation.
- U. S. 2,131,519, Sept. 27, 1938. M. Mizuta and T. Yoshimura. Sweetening cracked distillates with solutions of heavy metal naphthenates in volatile organic solvents.
- U. S. 2,131,525, Sept. 27, 1938. W. A. Schulze. Sweetening cracked distillates with copper chloride solution, followed by filtering through hair felt in order to improve coalescence of the aqueous phase.
- U. S. 2,138,566, Nov. 29, 1938. W. L. Benedict. Copper compounds are removed from copper-sweetened distillates with solid double sulfides of zinc and sodium.
- U. S. 2,143,078, Jan. 10, 1939. A. L. Lyman, H. B. Nichols, and R. C. Mithoff. Cracked distillates are refined in the vapor phase with iron sulfide and then with hydrogen to convert the disulfides into hydrogen sulfide.
- U. S. 2,146,027, Feb. 7, 1939. C. L. Read and T. J. Broidrick. Regenerating spent sodium plumbite solutions with air.
- U. S. 2,146,353, Feb. 7, 1939. T. W. Rosebaugh. Desulfurizing hydrocarbon oils with anhydrous alcoholic potassium hydroxide solution.
- U. S. 2,149,035, Feb. 28, 1939. G. H. von Fuchs and L. E. Border. Cracked distillates are sweetened with metallic copper in the presence of sulfur dioxide.
- U. S. 2,150,149, Mar. 14, 1939. R. E. Burk and E. C. Hughes. Sodium polysulfide is used to reduce corrosiveness of gasolines.
- U. S. 2,150,170, Mar. 14, 1939. W. O. Keeling. Gasoline is contacted with fuller's earth and then with sodium plumbite solution, followed by fractionation.
- U. S. 2,151,721, Mar. 28, 1939. W. A. Schulze. Desulfurization of light petroleum distillates in the vapor phase by heating and refining with clay.
- U. S. 2,152,721, Apr. 4, 1939. D. L. Yabroff. Sweetening cracked distillates by extracting with solutions of alkali hydroxides in methyl and ethyl alcohols, followed by regeneration of the spent solutions with air.
- U. S. 2,152,722, Apr. 4, 1939. D. L. Yabroff and E. R. White. Sweetening hydrocarbon distillates by washing with potassium alpha-hydroxybutyrate solutions.
- U. S. 2,152,723, Apr. 4, 1939. D. L. Yabroff. Solutions of aliphatic diamino alcohols are used for extracting mercaptans from cracked distillates.
- U. S. 2,152,724, Apr. 4, 1939. D. L. Yabroff and E. R. White. Regeneration of spent solutions obtained in extracting mercaptans by steaming at elevated temperatures.
- U. S. 2,154,988, Apr. 18, 1939. M. Mizuta and T. Yoshimura. Copper oleate is employed for sweetening cracked distillates.
- U. S. 2,156,577, May 2, 1939. D. L. Yabroff and E. R. White. Sodium alpha-hydroxyvalerate or similar substances are added to sodium hydroxide solutions used for sweetening cracked distillates.
- U. S. 2,160,116, May 30, 1939. H. E. Bode. Glucose and hydrochloric acid are used to improve odor of oils containing mercaptans.
- U. S. 2,162,670, June 13, 1939. R. E. Burk and E. C. Hughes. Sweetening of cracked distillates with sodium hydroxide solution in the presence of lead.
- U. S. 2,163,312, June 20, 1939. W. A. Schulze. Sweetening cracked distillates by filtering them through fuller's earth impregnated with cupric sulfate and sodium chloride solutions.
- U. S. 2,164,665, July 4, 1939. T. H. Rogers and B. H. Shoemaker. Sweet-

- ening cracked distillates with sodium hydroxide solutions.
- U. S. 2,171,009, Aug. 29, 1939. H. Ros-
tin and K. Schuster. Oil vapors are
mixed with hydrogen or with carbon
monoxide and passed at 550-950° F.
over minette.
- U. S. 2,171,033, Aug. 29, 1939. F. E.
Kimball. Refining cracked distillates
in the vapor phase with a molten mix-
ture of zinc and ammonium chlorides.
- U. S. 2,174,810, Oct. 3, 1939. G. H. von
Fuchs and L. E. Border. Cracked dis-
tillates are sweetened with metallic
copper in the presence of hydrogen
chloride.
- U. S. 2,181,036-7, Nov. 21, 1939. V. W.
Wilson. Cracked distillates are sweet-
ened with alcoholic sodium hydroxide
solution in the presence of hydrogen
peroxide.
- U. S. 2,185,768, Jan. 2, 1940. W. W.
Johnstone. Cracked distillates are
sweetened with a lead oxide solution in
lead acetate in the presence of elemen-
tal sulfur.
- CHAPTER VI.—REFINING BY ADSORPTION.
- U. S. 59,177, Oct. 30, 1866. R. E. Camp-
bell. Petroleum distillates are treated
with dry burned clay, chalk, and so-
dium chloride.
- U. S. 74,698, Feb. 18, 1868. J. D. Kirk-
patrick. Kerosene is filtered through
separate layers of lime, wood ashes,
elm bark, charcoal, and sand.
- U. S. 77,959, May 19, 1868. R. A. Chese-
brough. Lubricating oils are filtered
through bone black.
- U. S. 583,779, June 1, 1897. J. R. Whit-
ing and W. A. Lawrence. Petroleum
distillates are treated in the vapor
phase with charcoal and lime water.
- U. S. 618,307, Jan. 24, 1899. A. Wendt-
land. Acid-treated petroleum residues
are decolorized by refining them with
a solution of soap and barium chloride,
and filtering through bone black im-
pregnated with alcohol.
- U. S. 664,017, Dec. 18, 1900. A. M. Ed-
wards. Distilling oils in contact with
diatomaceous earth.
- U. S. 665,925, Jan. 15, 1901. H. Nordt-
meyer. Petroleum oils are filtered
through a mixture of kieselguhr and
asbestos.
- U. S. 692,283, Feb. 4, 1902. J. N. Har-
ris. Powdered decolorizing material is
added to oil, and the mixture heated to
110-130° F. and aerated in the presence
of alcohol.
- U. S. 705,168, July 22, 1902. J. W.
Warren. Treating oils with lead ace-
tate, sulfuric acid, and clay.
- U. S. 864,753, Aug. 27, 1907. F. J.
Lothammer and C. Trocquenet. Petro-
leum is emulsified with saponine, the
emulsion partly distilled, and the residue
boiled with a solution of sodium sili-
cate, sodium carbonate, and saponine.
- U. S. 898,879, Sept. 29, 1908. T. Ma-
cherski and E. Koperski. Decolorizing
oils by filtering through bone black
mixed with sodium carbonate and zinc
powder.
- U. S. 1,070,435, Aug. 19, 1913. L. Felizat.
Displacing oil from spent adsorbents
with aqueous solutions of sodium chlo-
ride, sodium sulfate, and sulfuric acid.
- U. S. 1,075,481, Oct. 14, 1913. D. F.
Lasher. Oil is filtered through the ash
of rice hulls.
- U. S. 1,114,095, Oct. 20, 1914. C. Bas-
kerville. Decolorizing oils with an or-
ganic and an inorganic adsorbent and
with an electrolyte.
- U. S. 1,132,054, Mar. 16, 1915. M. J.
Welsh. Treating burned regenerated
clays with acid to remove the fused
substances and to activate the clay.
- U. S. 1,221,698, Apr. 3, 1917. D. T. Day.
Distilling oil in the presence of sulfur
and passing the vapors through adsor-
bent materials.
- U. S. 1,337,523, Apr. 20, 1920. E. H.
Leslie and C. Barbre. Decolorizing
and neutralizing oils by treating with
a mixture of an adsorbent material and
a neutralizing agent, like calcium oxide,
calcium carbonate, or sodium carbonate.
- U. S. 1,356,631, Oct. 26, 1920. C. F.
Kennedy. Recovering oil from spent
adsorbents with solutions of sulfonated
soaps.
- U. S. 1,423,064. O. P. Amend. Motor
fuels are prepared by cracking petro-
leum vapors in the presence of carbon,
clay, metal filings, or metallic oxides.
- U. S. 1,504,772, Aug. 12, 1924. F. W.
Manning. Treating petroleum oils with
sulfur's



- earth from percolation filters by successive washes with naphtha.
- U. S. 1,507,692, Sept. 9, 1924. F. H. Smith and G. J. Ziser. Aging the oil before treating with adsorbents.
- U. S. 1,579,326, Apr. 6, 1926. H. L. Kauffman. Using the acid-treated mineral, leverrierite, for decolorizing oils.
- U. S. 1,600,845, Sept. 21, 1926. H. Reinbold. Treating oils with bentonite, sodium hydroxide, and chlorine.
- U. S. 1,603,314, Oct. 19, 1926. L. Caldwell. Treating oil with lime and then with diatomaceous earth.
- U. S. 1,628,747, May 17, 1927. O. J. Salisbury. Treating oils with clay in a countercurrent manner.
- U. S. 1,633,871, June 28, 1927. P. W. Prutzman. Regenerating spent clays with naphtha and alcohol, followed by water washing.
- U. S. 1,647,459, Nov. 1, 1927. E. B. Miller. Sweetening gasoline by exposing it to actinic light and treating with an absorbent.
- U. S. 1,699,989, Jan. 22, 1929. D. Pyzel. Oils are distilled in the presence of inert porous material, steam, and oxygen.
- U. S. 1,715,535, June 4, 1929. M. L. Chappell. Regeneration of adsorbents by washing with oil and sulfuric acid to which acetone, alcohol, or gasoline may be added, followed by washing with acetone, alcohol and gasoline.
- U. S. 1,718,672, June 25, 1929. C. A. Ward. Separating wax from oils by mixing them with adsorbents, chilling, and filtering.
- U. S. 1,734,959, Nov. 12, 1929. J. C. Black. Apparatus for treating oils with clays.
- U. S. 1,752,455, Apr. 1, 1930. A. G. Peterkin, Jr. Treating cracked gasoline in the vapor phase with fuller's earth, which is introduced into the still with a reflux oil.
- U. S. 1,753,859, Apr. 8, 1930. T. T. Gray. Treating cracked gasoline vapors by passing them through separate layers of adsorbents.
- U. S. 1,763,167, June 10, 1930. H. Lowery. Displacing oil from spent adsorbents with sodium carbonate solution.
- U. S. 1,770,166, July 8, 1930. F. A. Bent. Use of poly-alcohols, their esters, or ethers for recovery of spent clays.
- U. S. 1,782,744, Nov. 25, 1930. W. D. Rial and W. R. Barratt. Spent clay is washed with naphtha and then with a solvent obtained from sulfuric acid sludge after separation of water-soluble constituents.
- U. S. 1,786,493, Dec. 30, 1930. E. W. Isom and E. B. Phillips. Refining viscous oils by mixing them with adsorbents and heating to a temperature below cracking.
- U. S. 1,788,653-4, Jan. 13, 1931. W. S. Baylis. Decolorization of lubricating oils by mixing them with adsorbents, heating, and fractionating the oil.
- U. S. 1,792,625, Feb. 17, 1931. W. S. Baylis. Preparation of a decolorizing clay by heating to remove free water and water of crystallization and treating with anhydrous sulfuric acid.
- U. S. 1,792,877, Feb. 17, 1931. W. M. Stratford. Treating cracked gasoline with adsorbents in the vapor phase.
- U. S. 1,793,885, Feb. 24, 1931. C. B. Watson and R. C. Osterstrom. Vapor phase refining with fuller's earth.
- U. S. 1,795,067, Mar. 3, 1931. F. A. Appgar. Treatment of cracked gasoline in the vapor phase with adsorbents.
- U. S. 1,796,310, Mar. 17, 1931. W. O. Stevens. Lubricating oils are refined with wood ash.
- U. S. 1,796,799, Mar. 17, 1931. R. E. Manley and M. L. Langworthy. Preparation of a decolorizing clay by treating it with 10% sulfuric acid solution.
- U. S. 1,797,255, Mar. 24, 1931. F. A. Appgar. Treatment of cracked distillates in the vapor phase with fuller's earth.
- U. S. 1,797,262, Mar. 24, 1931. E. C. Herthel. Apparatus for vapor-phase treatment of oils with adsorbents.
- U. S. 1,797,513, Mar. 24, 1931. R. C. Osterstrom and R. T. Tucker. Apparatus for vapor-phase treatment of light oils with adsorbents.
- U. S. 1,801,942, Apr. 21, 1931. R. K. Stratford and G. McIntyre. Regeneration of Attapulgis fuller's earth by extracting with naphtha and then with a mixture of alcohol and benzene.
- U. S. 1,803,941, May 5, 1931. E. R. Lederer. Residual lubricating oils are

- aged, treated with sulfuric acid at about 120° F., settled, treated with clay at about 420° F., and dewaxed.
- U. S. 1,805,178, May 12, 1931. N. E. Lemmon. Revivification of spent fuller's earth by washing with a mixture of naphtha, benzene, and alcohol.
- U. S. 1,806,020, May 19, 1931. C. K. Parker and F. A. Bent. Regeneration of spent clay by burning in the presence of air and steam.
- U. S. 1,806,876, May 26, 1931. D. W. Grant. Decolorization of lubricating oils by treatment with fuller's earth on a filter.
- U. S. 1,809,862, June 16, 1931. A. R. Moorman and I. C. Carpenter. Treatment of lubricating oils with sulfuric acid, followed by treatment first with partially spent and then with fresh adsorbents.
- U. S. 1,810,155, June 16, 1931. W. S. Baylis. Reactivation of spent adsorbents by roasting and then mixing with sulfuric acid solution of 1-4% strength.
- U. S. 1,811,185, June 23, 1931. R. C. Osterstrom. Decolorization of lubricating oils by contacting with clays at elevated temperatures.
- U. S. 1,812,426, June 30, 1931. F. A. Apgar. Cracked gasoline vapors are mixed with steam or gaseous hydrocarbons and passed through fuller's earth.
- U. S. 1,812,446, June 30, 1931. W. Mendius. Apparatus for refining hydrocarbon vapors with fuller's earth.
- U. S. 1,812,923, July 7, 1931. W. T. Bryant. Treatment of lubricating oils with sulfuric acid, drawing the sludge, and contacting the oil with adsorbents at 212° F.
- U. S. 1,817,968, Aug. 11, 1931. R. Cross. Revivifying with chlorine bentonite used in refining oils.
- U. S. 1,818,274, Aug. 11, 1931. P. W. Prutzman. Treating lubricating oils by contacting with adsorbents at elevated temperatures.
- U. S. 1,822,303, Sept. 8, 1931. E. B. Miller. Revivification of silica gel by heating in the presence of a non-oxidizing gas (steam, carbon dioxide, or nitrogen) and then with air.
- U. S. 1,823,175, Sept. 15, 1931. J. G. Stafford. Refining cracked distillates by blending with kerosene and treating with clay at elevated temperatures and under pressure.
- U. S. 1,823,895, Sept. 22, 1931. T. T. Gray. Apparatus for treating light distillates in the vapor phase with fuller's earth.
- U. S. 1,823,994, Sept. 22, 1931. W. M. Stratford. Decolorization of lubricating oils by distillation under reduced pressure in the presence of adsorbents.
- U. S. 1,825,300, Sept. 29, 1931. W. S. Baylis. Decolorizing gasoline by filtering through blotting paper into which 10-25% of Filtrol, containing 0.15-0.50% of sulfuric acid, has been incorporated.
- U. S. 1,825,330, Sept. 29, 1931. C. R. Baker. Filtering oil-clay mixtures by precoating the filter with diatomaceous earth.
- U. S. 1,827,165, Oct. 13, 1931. J. K. Pfaff. Recovering spent clays by heating under pressure with dilute sulfuric acid.
- U. S. 1,830,962, Nov. 10, 1931. C. D. Read and R. L. Holcomb. Filtering petroleum tars through clays.
- U. S. 1,832,892, Nov. 24, 1931. J. C. Black. Apparatus for treating lubricating oils with contact clays.
- U. S. 1,836,577, Dec. 15, 1931. R. Cross. Preparation of an adsorbent material from hydrous aluminum silicate and copper.
- U. S. 1,836,947, Dec. 15, 1931. W. S. Zehrung. Distillation of crude oils in the presence of adsorbents.
- U. S. 1,838,621, Dec. 29, 1931. J. D. Haseman. Preparation of bleaching clay by treating with sulfuric acid.
- U. S. 1,839,388, Jan. 5, 1932. T. T. Gray. Refining cracked gasoline in the vapor phase with fuller's earth.
- U. S. 1,840,158, Jan. 5, 1932. R. Cross. Refining gasoline in the vapor phase by passing vapors through copper, iron, or manganese compounds having an affinity for sulfur, and then through fuller's earth.
- U. S. 1,840,164, Jan. 5, 1932. J. H. Hirt. Removing colloidal or emulsified substances by filtering oils through compressed porous volcanic ash.
- U. S. 1,841,271, Jan. 12, 1932. F. A. Apgar. Passing lubricating oil vapors

- through fuller's earth at a pressure below 20 inches of mercury.
- U. S. 1,844,476, Feb. 9, 1932. J. C. Morrell. Preparation of adsorbents by treating fuller's earth with hydrofluoric acid.
- U. S. 1,847,623, Mar. 1, 1932. T. F. Ott. Treatment of lubricating oils with 40-90% sulfuric acid and then with sodium hydroxide solution or clay.
- U. S. 1,847,778, Mar. 1, 1932. M. Melamid. Treating crude oil with kieselguhr which is impregnated with dilute sulfuric acid and dried.
- U. S. 1,849,653, Mar. 15, 1932. W. S. Baylis. Treating petroleum oils with spent adsorbents in the presence of steam and then with fresh adsorbents under vacuum.
- U. S. 1,851,627, Mar. 29, 1932. H. J. Hartley. Mixing fresh or spent adsorbents with water before calcining to insure formation of pores.
- U. S. 1,852,603, Apr. 5, 1932. G. G. Brockway. Spent contact clay is freed from oil by washing with hydrocarbon solvents, mixed with coarse or granular material, and revived by burning.
- U. S. 1,853,671, Apr. 12, 1932. E. A. Dickinson. Cracked distillates are refined with fuller's earth in the vapor phase by employing gasoline as a reflux medium to control the boiling range of the product.
- U. S. 1,853,972, Apr. 12, 1932. T. T. Gray. Vapor-phase treatment with adsorbents in an apparatus permitting recovery of heat from the outgoing vapors.
- U. S. 1,856,934, May 3, 1932. J. G. Stafford. Lubricating oils are decolorized by contacting with clay for 2-5 minutes at 500-600° F. in an atmosphere of a reducing gas, such as pressure still gases.
- U. S. 1,858,110, May 10, 1932. H. Pease. In vapor-phase refining with fuller's earth the pressure differential through the adsorptive material is periodically increased by reducing the pressure applied to the exit vapors.
- U. S. 1,862,507, June 7, 1932. T. T. Gray. Apparatus for refining cracked distillates in the vapor phase with fuller's earth.
- U. S. 1,865,467, July 5, 1932. T. T. Gray. In vapor-phase refining with fuller's earth the hydrocarbon vapors are passed through the earth with a velocity sufficient to carry polymers out of the earth bed.
- U. S. 1,866,590, July 12, 1932. W. S. Baylis. Lubricating oils are decolorized by mixing with water, followed by addition of clay and heating under pressure to elevated temperatures, but below the flash point of the oil. The oil is then treated with additional quantities of clay to effect final decolorization.
- U. S. 1,866,591, July 12, 1932. W. S. Baylis. Lubricating oil is treated with contact clays at elevated temperatures, the mixture is slowly cooled, and the oil extracted from the cool mass with a hydrocarbon solvent.
- U. S. 1,872,988, Aug. 23, 1932. E. R. Lederer. Used clay is recovered by leaching with hydrocarbon solvents, re-filtering to remove the entrapped oil and hydrocarbon solvent, drying and finally heating to a sufficiently high temperature to effect revivification.
- U. S. 1,873,783, Aug. 23, 1932. R. C. Osterstrom and R. T. Tucker. Petroleum distillates are freed from color and gum-forming constituents by contacting their vapors with fuller's earth. The gasoline vapors are then passed countercurrently to a stream of liquid hydrocarbon materials to remove the polymers and high-boiling materials.
- U. S. 1,881,217, Oct. 4, 1932. H. H. Moreton. Hydrocarbon oils are contacted with a mixture of clay and silica impregnated with sulfuric acid.
- U. S. 1,884,495, Oct. 25, 1932. P. Zurcher. Petroleum distillates are purified by passing their vapors over activated carbon at 750-1000° F.
- U. S. 1,884,587, Oct. 25, 1932. H. T. Darlington. Lubricating oils are treated under vacuum with bentonite in colloid dispersion and at 500-850° F. in contact with air.
- U. S. 1,886,260, Nov. 1, 1932. E. B. Miller. Hydrocarbon distillates are purified with silica gel impregnated with sulfuric, phosphoric, or nitric acid.
- U. S. 1,887,018, Nov. 8, 1932. A. E. Harnsberger. Vapor-phase cracked

- gasoline is freed from gum-forming constituents by contacting with fuller's earth in the vapor phase.
- U. S. 1,888,346, Nov. 22, 1932. H. T. Darlington. Lubricating oils are purified by heating them under pressure with adsorbents. The lighter fractions are separated, and the residual fraction is further treated with adsorbents.
- U. S. 1,890,255, Dec. 6, 1932. I. K. Fuller. Spent clay is revived by washing with gasoline, drying, extracting with a mixture of benzol and methyl-ethyl ketone, filtering, and washing with fresh solvent to separate the residual adsorbed material.
- U. S. 1,890,284, Dec. 6, 1932. I. K. Fuller. Spent adsorbents are freed from oil by mixing with gasoline, filtering, and treating the filter cake with a solvent to remove the remaining dilute oil solution.
- U. S. 1,891,106, Dec. 13, 1932. R. C. Osterstrom. Vapor-phase refining of cracked distillates with fuller's earth.
- U. S. 1,891,107, Dec. 13, 1932. R. C. Osterstrom. Apparatus for refining cracked distillates with fuller's earth at elevated temperatures and pressures.
- U. S. 1,891,108, Dec. 13, 1932. R. C. Osterstrom and C. R. Wagner. Apparatus for refining cracked distillates with fuller's earth at elevated temperatures by refluxing for a sufficient length of time to effect polymerization of the undesirable constituents.
- U. S. 1,891,109, Dec. 13, 1932. R. C. Osterstrom. Removing color compounds and gum-forming constituents from cracked products by heating them under pressure with fuller's earth and then releasing the pressure to effect vaporization.
- U. S. 1,891,402, Dec. 20, 1932. F. L. Craise, H. G. Vesper, and H. G. Griffith. Refining oils by treatment with fuller's earth at elevated temperatures. The pressure is varied to expel the water.
- U. S. 1,894,323, Jan. 17, 1933. R. C. Osterstrom. Continuous process for refining and decolorizing oils with adsorbents, such as fuller's earth, by heating under pressure with adsorbents, followed by vaporization of the oil from the adsorbent.
- U. S. 1,894,331, Jan. 17, 1933. C. B. Watson. Color substances and gum-forming constituents are removed by heating cracked distillates with fuller's earth at elevated temperatures and under pressure, followed by fractionation.
- U. S. 1,895,062, Jan. 24, 1933. P. Zurcher. Oils are refined with activated carbon produced from petroleum coke. The carbon is regenerated with steam at about 565° F.
- U. S. 1,897,328, Feb. 14, 1933. R. C. Osterstrom. Treatment of cracked distillates with fuller's earth at elevated temperatures and under pressure.
- U. S. 1,897,389, Feb. 7, 1933. A. E. Harnsberger and A. L. Christy. Apparatus for refining oils with fuller's earth.
- U. S. 1,898,165, Feb. 21, 1933. W. S. Baylis and D. S. Belden. Contact clay is wetted with water, mixed with oil, and allowed to stand until the water is adsorbed by the clay, then heated to 120-400° F., and further decolorized with additional clay at lower temperatures.
- U. S. 1,898,168, Feb. 21, 1933. D. S. Belden. Oils are decolorized with adsorbent clays in the presence of carbon dioxide or nitrogen.
- U. S. 1,903,094, Mar. 28, 1933. M. S. Darrow and L. S. Swecney. Decolorizing and neutralizing acid-treated oils by passing them through a mixture of fuller's earth, sodium hydroxide, and lead oxide.
- U. S. 1,904,183, Apr. 18, 1933. A. A. Wells. Decolorizing lubricating oils by agitating with clay at not less than 220° F.
- U. S. 1,904,682, Apr. 18, 1933. I. K. Fuller. Decolorizing oils by filtering them through adsorbents, collecting the filtrate in a plurality of superimposed layers, and recirculating it through the adsorbents progressively from the lightest colored oil to the darkest.
- U. S. 1,908,599, May 9, 1933. T. T. Gray. Refining cracked distillates by passing their vapors through several separate layers of fuller's earth and separating the polymers after each passage.

- U. S. 1,908,606, May 9, 1933. E. C. Herthel. Refining cracked distillates by passing their vapors through a bed of fuller's earth with refluxing of some of the hydrocarbons.
- U. S. 1,911,830, May 30, 1933. R. B. Lebo. Adsorbent clays are prepared by heating them to remove moisture, impregnating the hot dry clay with oil, and then cooling the mixture.
- U. S. 1,913,960, June 13, 1933. E. E. Roll. Clay for oil refining is prepared by treating it with sulfuric acid, washing, treating with hydrochloric acid, washing, and drying.
- U. S. 1,915,433, June 27, 1933. M. D. Mann, Jr. and F. M. Archibald. Apparatus for treating lubricating oils with clays and recovering the adsorbed oil by washing the clay with large quantities of water.
- U. S. 1,920,922, Aug. 1, 1933. H. N. Lyons. Lubricating oils are refined and decolorized by mixing them with clay and water, heating to vaporize the water, and chilling and filtering the oil from the wax and clay.
- U. S. 1,929,861, Oct. 10, 1933. J. B. Weaver. Apparatus for treating cracked distillates with finely divided adsorbents for removing gum- and color-forming constituents at elevated temperatures.
- U. S. 1,929,907, Oct. 10, 1933. H. Thomas. Apparatus for refining gasoline with fuller's earth.
- U. S. 1,930,453, Oct. 10, 1933. J. W. Brown. Refining cracked distillates with fuller's earth in the vapor phase.
- U. S. 1,930,597, Oct. 17, 1933. R. C. Osterstrom and R. T. Tucker. Apparatus for refining oils with fuller's earth.
- U. S. 1,930,974, Oct. 17, 1933. F. W. Hall and J. H. Grahame. Refining cracked gasolines in the vapor phase with fullers' earth, followed by fractionation.
- U. S. 1,934,967, Nov. 14, 1933. A. G. Connolly. Apparatus for refining cracked distillates in the vapor phase with fuller's earth.
- U. S. 1,934,968, Nov. 14, 1933. A. G. Connolly. Apparatus for refining cracked distillates with fuller's earth in the vapor phase.
- U. S. 1,937,113, Nov. 28, 1933. T. T. Gray. Cracked distillates are refined in the vapor phase with fuller's earth and copper oxide.
- U. S. 1,938,998, Dec. 12, 1933. A. G. Connolly. Apparatus for vapor-phase refining with fuller's earth.
- U. S. 1,943,976, Jan. 16, 1934. G. R. Lewers. Kiln for revivifying fuller's earth.
- U. S. 1,944,877, Jan. 30, 1934. H. T. Darlington. Refining oil vapors with fuller's earth or bog iron ore in colloidal dispersion.
- U. S. 1,945,215, Jan. 30, 1934. A. E. Buell. Spent clays are revivified by agitating with a mixture of naphtha and an alcoholic solution of sodium hydroxide.
- U. S. 1,945,249, Jan. 30, 1934. M. P. Youker. Apparatus for treating hydrocarbon vapors with fuller's earth.
- U. S. 1,945,583, Feb. 6, 1934. R. Wietzel and B. Engel. Finely divided impurities are removed from hydrocarbon oils by filtering them through finely divided carbonaceous residues.
- U. S. 1,946,095, Feb. 6, 1934. J. C. Morrell and G. Egloff. Cracked distillates are refined by passing their vapors over phosphoric acid and fuller's earth.
- U. S. 1,946,748, Feb. 13, 1934. N. E. Lemmon and A. B. Brown. Clays are revivified by washing them with naphtha, removing the residual solvent with the aid of hydrocarbon gases, and "burning" the clay.
- U. S. 1,947,868, Feb. 20, 1934. J. C. Morrell and G. Egloff. Cracked distillates are refined by mixing their vapors with sulfur dioxide, oxygen, and steam, and contacting with bauxite, fuller's earth, or zeolite.
- U. S. 1,948,126, Feb. 20, 1934. P. S. Nisson. Apparatus for contacting hydrocarbon vapors with fuller's earth.
- U. S. 1,949,673, Mar. 6, 1934. W. S. Baylis. Cracked distillates are refined in the vapor phase with finely divided adsorbents, such as acid-treated clays, and separating the adsorbents from the oil by electrical precipitation.
- U. S. 1,949,749, Mar. 6, 1934. C. D. Lowry. Cracked distillates are treated in the vapor phase with greensand,

- preferably in the presence of hydrochloric acid.
- J. S. 1,950,140, Mar. 6, 1934. A. M. Gray. Apparatus for refining cracked distillates with fuller's earth in the vapor phase.
- J. S. 1,951,120, Mar. 13, 1934. F. A. Apgar and K. A. Beach. Cracked distillates are refined with fuller's earth in the vapor phase.
- J. S. 1,952,482, Mar. 27, 1934. H. Whitaker. Petroleum distillates containing organic sulfides are purified in the vapor phase with silica gel.
- J. S. 1,952,855, Mar. 27, 1934. T. T. Gray. Cracked distillates are contacted in the vapor phase with fuller's earth, and polymers are removed by passing the vapors through a heavier hydrocarbon oil.
- U. S. 1,956,716, May 1, 1934. J. Hansen. Acid-treated distilled lubricating oil stock is mixed with fuller's earth and heated to 300° F. under vacuum.
- U. S. 1,957,449, May 8, 1934. D. M. Evans and W. C. Dorsett. Cracked distillates are purified by heating them with fuller's earth under pressure.
- U. S. 1,957,794, May 8, 1934. J. C. Morrell and G. Egloff. Cracked distillates are refined by passing their vapors mixed with ozone through fuller's earth and sodium hydroxide solution.
- U. S. 1,960,561, May 29, 1934. J. M. Wadsworth. Apparatus for contacting hydrocarbon vapors with fuller's earth.
- U. S. 1,962,752. W. M. Stratford. Refining cracked distillates in vapor phase with fuller's earth.
- U. S. 1,965,105, July 3, 1934. M. R. Mandelbaum. Refining cracked distillates with fuller's earth in the vapor phase, first with partially spent and then with fresh adsorbent.
- U. S. 1,970,796, Aug. 21, 1934. G. A. Beiswenger. Refining lubricating oils in the course of distillation with Filtrol.
- U. S. 1,974,089, Sept. 18, 1934. C. Tietig. Oil is decolorized with contact clays while agitated with gaseous sulfur trioxide.
- U. S. 1,976,000, Oct. 9, 1934. F. A. Apgar and K. A. Beach. Apparatus for refining gasoline and kerosene in vapor phase with fuller's earth.
- U. S. 1,976,177, Oct. 9, 1934. A. Lazar. Stability of transformer and lubricating oils is improved by treating them with clay at elevated temperatures in contact with air and steam.
- U. S. 1,980,119, Nov. 6, 1934. J. F. Wait. Spent clay is mixed with a filler and treated with ozone to make it suitable for manufacturing wall- or roof-lining sheets.
- U. S. 1,980,431, Nov. 13, 1934. I. M. Perkins. Fuller's earth is first wetted with the same oil which is to be percolated through it.
- U. S. 1,986,228, Jan. 1, 1935. J. D. Seguy. Cracked distillates are contacted in the vapor phase with an adsorbent containing triethanolamine.
- U. S. 1,987,175, Jan. 8, 1935. V. C. Benjamin. Apparatus for refining lubricating oils with clay.
- U. S. 1,989,330, Jan. 29, 1935. M. M. Moore, R. R. Thorburn, and W. B. Wilson. Refining lubricating oils with finely divided acid-treated clays.
- U. S. 1,990,608, Feb. 12, 1935. O. D. Lucas and E. J. Lush. Apparatus for refining hydrocarbon vapors with fuller's earth.
- U. S. 1,992,979, Mar. 5, 1935. H. J. Wollner. Purifying oils by contacting them with activated silica.
- U. S. 1,997,174, Apr. 9, 1935. H. H. Gross. Spent clays are regenerated by heating them under pressure with furfural.
- U. S. 1,997,938, Apr. 16, 1935. N. E. Loomis. Oil is heated, mixed with finely divided clay, and fractionated.
- U. S. 1,999,335, Apr. 30, 1935. P. J. McDermott. Gasoline is filtered through fuller's earth containing ferric sulfate and free sulfuric acid.
- U. S. 2,000,672, May 7, 1935. R. K. Stratford and C. Leaver. Gasoline vapors are treated countercurrently with clay.
- U. S. 2,006,088, June 25, 1935. E. R. Mitchell. Oil is separated from spent clay by heating the spent oil-clay mixture with brine.
- U. S. 2,007,242, July 9, 1935. N. G. de Rachat. Revivification of fine spent clay by means of hot gases.
- U. S. 2,013,083, Sept. 3, 1935. M. J. Welsh. Cracked gasoline is refined

- with an adsorbent, heated to remove hydrogen sulfide, washed with water, and sweetened.
- U. S. 2,016,271, Oct. 8, 1935. A. E. Buell and W. A. Schulze. Cracked distillates are sweetened by contacting their vapors with bauxite.
- U. S. 2,019,184, Oct. 29, 1935. T. T. Gray. Desulfurizing gasoline by treating in the vapor phase with fuller's earth at 554-842° F.
- U. S. 2,020,115, Nov. 5, 1935. T. T. Gray. Cracked gasoline is treated in the vapor phase with fuller's earth, the upward velocity of the vapors being sufficient to retard the fall of clay particles in the upper portion of the treating chamber.
- U. S. 2,020,954, Nov. 12, 1935. J. M. Musselman. Refining lubricating oils with a mixture of aluminum chloride and fuller's earth.
- U. S. 2,022,358, Nov. 26, 1935. C. R. McKay and J. H. Smith. Acid-treated oil is partially neutralized with calcium hydroxide and then contacted with fuller's earth.
- U. S. 2,024,589, Dec. 17, 1935. G. R. Lewers. Apparatus for regeneration of spent adsorbents by burning.
- U. S. 2,027,410, Jan. 14, 1936. H. M. Weir. Vapor-phase treatment of oils with fuller's earth supported on steel wool.
- U. S. 2,028,100, Jan. 14, 1936. R. J. Dearborn and W. M. Stratford. Refining oils in the vapor phase with fuller's earth.
- U. S. 2,028,995, Jan. 28, 1936. F. M. Rogers. Refining gasoline in the vapor phase with fuller's earth, followed by washing the condensate with sodium hydroxide solution.
- U. S. 2,035,440, Mar. 31, 1936. F. M. Archibald and P. Janssen. Refining light distillates in the vapor phase with bauxite, kaolin, or silica gel.
- U. S. 2,036,166, Mar. 31, 1936. A. A. Wells. Refining naphtha with a clay-water slurry at elevated temperatures.
- U. S. 2,038,604, Apr. 28, 1936. L. H. Robertson and W. A. Eberle. Lubricating oils in naphtha solution are percolated through a partially exhausted clay, and then the naphtha removed from the oil and the oil percolated through fresh clay.
- U. S. 2,039,239, Apr. 28, 1936. C. W. Watson. Stabilizing the color of cracked distillates by contacting their vapors with adsorbent material and a treated liquid hydrocarbon material.
- U. S. 2,039,576, May 5, 1936. G. W. Ayers, Jr. Cracked distillates are stabilized by contacting them in the vapor phase with fuller's earth and adding to the product a small quantity of an aminobenzene, such as di-methyl or di-ethyl aniline.
- U. S. 2,039,595, May 5, 1936. J. Hyman and G. W. Ayers, Jr. Cracked distillates are stabilized by contacting them in the vapor phase with fuller's earth and adding to the product a small quantity of para-aminophenol.
- U. S. 2,043,016, June 2, 1936. W. M. Stratford. Cracked distillates are refined in the vapor phase with fuller's earth or activated charcoal.
- U. S. 2,045,160, June 23, 1936. A. R. Moorman and I. C. Carpenter. Oil is passed through a heating chamber to distill the lighter fractions, and the residuum is immediately contacted with a decolorizing clay.
- U. S. 2,054,774, Sept. 15, 1936. R. E. Manley and W. Ullrich. Refining cracked distillates in the vapor phase with finely divided acid-treated clays.
- U. S. 2,055,616, Sept. 29, 1936. J. V. Starr. Adsorbent clays are revived by extraction with a sulfur dioxide kerosene extract mixed with methyl-ethyl ketone.
- U. S. 2,065,643, Dec. 29, 1936. D. G. Brandt. Spent fuller's earth is revived by "burning" it in a stream of air.
- U. S. 2,067,334, Jan. 12, 1937. R. C. Osterstrom. Preparation of motor fuels and lubricants from vapor-phase cracked distillate by treatment with fuller's earth or charcoal, followed by refining the viscous distillate fraction from the polymers with sulfuric acid.
- U. S. 2,077,494, Apr. 20, 1937. E. R. Smoley. Refining cracked distillates in the vapor phase with fuller's earth.
- U. S. 2,079,158, May 4, 1937. N. G. de Rachat. Continuous refining of cracked distillate in the vapor phase with clays.

- U. S. 2,079,782, May 11, 1937. A. A. Wells. Refining oils with clay, followed by agitation with moist sulfur dioxide.
- U. S. 2,079,934, May 11, 1937. L. H. Fitch, Jr., and F. E. Frey. Refining gasoline in the vapor phase with fuller's earth.
- U. S. 2,084,510, June 22, 1937. J. C. Showalter. Decolorizing and imparting bloom to lubricating oils with a spent clay which has been heated to the incipient cracking of the adsorbed oil.
- U. S. 2,087,048, July 13, 1937. W. A. Schulze. Cracked distillates are desulfurized in the vapor phase with bauxite.
- U. S. 2,087,525, July 20, 1937. J. C. Morrell and G. Egloff. Cracked distillates are refined in the vapor phase with hydrogen chloride, steam, and oxygen in the presence of an activated clay.
- U. S. 2,089,655, Aug. 10, 1937. F. H. MacLaren. Decolorization of pour point depressants with fuller's earth.
- U. S. 2,090,159, Aug. 17, 1937. H. A. Smith. Refining cracked distillates in the vapor phase with fuller's earth by introducing into the clay bed a solvent for the polymers.
- U. S. 2,096,820, Oct. 26, 1937. E. F. Nelson. Refining cracked distillates in the vapor phase with fuller's earth.
- U. S. 2,096,909, Oct. 26, 1937. M. Maxwell. Imparting fluorescence to lubricating oils by adding a residuum which has been contacted with clay for several hours at elevated temperatures.
- U. S. 2,097,097, Oct. 26, 1937. W. T. Hancock. Refining cracked distillates in the liquid phase at elevated temperatures and under pressure with fuller's earth and an oxygen-containing gas.
- U. S. 2,106,071, Jan. 18, 1938. R. E. Stanton. Deasphalting lubricating oils with propane, followed by percolation of the propane solution through clay.
- U. S. 2,107,215, Feb. 1, 1938. E. W. Renihert. Percolation medium is prepared from a mixture of decolorizing clay and magnesium silicate.
- U. S. 2,107,354, Feb. 8, 1938. J. M. Wadsworth. Apparatus for refining oils in the vapor phase with fuller's earth.
- U. S. 2,108,690, Feb. 15, 1938. H. S. Montgomery. Apparatus for refining cracked distillates in the vapor phase with fuller's earth.
- U. S. 2,113,010, Apr. 5, 1938. C. F. Tears. Spent clays are regenerated by successive extraction with acetylene dichloride and liquid propane.
- U. S. 2,116,220, May 3, 1938. B. H. Shoemaker. Improving the stability of wax by percolating the molten wax through clay and adding *tert*-butyl catechol.
- U. S. 2,118,310, May 24, 1938. H. L. Kauffman. Clay is heated to at least 1425° F. for 4-5 seconds and quickly cooled with water in order to improve its decolorization efficiency.
- U. S. 2,121,518, June 21, 1938. F. W. Breth and A. Kinsel. Petrolatum is filtered through bauxite.
- U. S. 2,127,654, Aug. 23, 1938. R. K. Stratford. Refining cracked distillates in the vapor phase with fuller's earth.
- U. S. 2,128,931, Sept. 6, 1938. S. W. Ferris and H. C. Cowles, Jr. Spent clays are revived by extraction with acetone or alcohol, followed by extraction with naphtha or carbon disulfide.
- U. S. 2,134,824, Nov. 1, 1938. W. G. Hiatt. Refining cracked distillates in the vapor phase with a clay catalyst.
- U. S. 2,139,161, Dec. 6, 1938. G. H. Hutchins and A. W. Hartigan. Contacting lubricating oils with finely divided adsorbents in two stages.
- U. S. 2,144,276, Jan. 17, 1939. H. M. Steininger. Refining cracked distillates in the vapor phase with fuller's earth.
- U. S. 2,154,434, Apr. 18, 1939. G. R. Bond, Jr. Decolorization of lubricating oils with silica-alumina compositions shaped into pellets.
- U. S. 2,160,874, June 6, 1939. A. Kinsel. Regenerating bauxite by burning, followed by magnetic separation of the inert particles.
- U. S. 2,161,306, June 6, 1939. A. E. Miller and G. R. Lord. Regenerating contact clays with solvents.
- U. S. 2,162,319, June 13, 1939. W. A. Schulze. Cracked distillates are desulfurized in the vapor phase with bauxite.
- U. S. 2,162,715-7, June 20, 1939. W. T. Hancock. Refining cracked petroleum distillates with fuller's earth in the vapor phase.

- U. S. 2,170,628, Aug. 22, 1939. F. W. Breth. Lubricating oils are percolated through bauxite.
- U. S. 2,170,976, Aug. 22, 1939. M. P. Youker. Hydrocarbon vapors are refined with fuller's earth.
- U. S. 2,171,377, Aug. 29, 1939. C. F. Tears. Filtering lubricating oils in propane solution and under pressure through adsorbent clays.
- U. S. 2,172,436, Sept. 12, 1939. H. B. Cooke and M. R. Mandelbaum. Refining gasoline with fuller's earth in the vapor phase followed by contacting the vapors with a hydrocarbon solvent.
- U. S. 2,180,220, Nov. 14, 1939. G. A. Boyd. Preparation of acid-treated fuller's earth.
- CHAPTER VII.—REFINING WITH SOLVENTS.
- U. S. 101,284, Mar. 29, 1870. O. Loew. Washing oils with water before acid treatment.
- U. S. 507,230, Oct. 24, 1893. R. H. Laird. Treating oil vapors by passing them through sodium chloride, sand, and calcium hypochlorite.
- U. S. 557,291, Mar. 31, 1896. A. J. Tempère. Kerosene is treated with amyl acetate.
- U. S. 1,152,478, Sept. 7, 1915. J. C. Black. Treating oils with gaseous sulfur dioxide.
- U. S. 1,396,399, Nov. 8, 1921. O. E. Bransky. Purifying acid-treated oils by extracting with a solution of a sulfonated mineral oil.
- U. S. 1,526,534, Feb. 17, 1925. R. A. Dornes. Purifying oils by mixing their vapors with steam and alcohol before condensation.
- U. S. 1,550,523, Aug. 18, 1925. E. Eichwald. Separating aromatics from the oil by extracting them with furfural.
- U. S. 1,562,425, Nov. 17, 1925. A. Greenspan. Separation of wax from lubricating oil by adding 15-20% kerosene to the lubricating oil, cooling, filtering, and distilling out the kerosene.
- U. S. 1,585,473, May 18, 1926. L. Edeleanu. Extracting light petroleum distillates with liquid sulfur dioxide and blending the extract with motor fuels.
- U. S. 1,651,328, Nov. 29, 1927. L. Edeleanu, K. Pfeiffer, K. Gress, and P. Jodeck. Apparatus for treating oils with liquid sulfur dioxide.
- U. S. 1,668,275, May 1, 1928. W. Hess. Saturating the oil with gaseous sulfur dioxide before treating with liquid sulfur dioxide.
- U. S. 1,674,676, June 26, 1928. W. Hess. Treating oils in two steps with liquid sulfur dioxide.
- U. S. 1,680,352-3, Aug. 14, 1928. T. A. Werkenthin. Fractional extraction of lubricating oils with alcohol.
- U. S. 1,683,288, Sept. 4, 1928. F. W. Eley. Removing polymerized substances from mineral oils with a solution of glacial acetic acid and ether.
- U. S. 1,683,767, Sept. 11, 1928. G. Egloff. Separation of carbonaceous material from cracked residuum by diluting with light distillates and centrifuging.
- U. S. 1,706,120, Mar. 19, 1929. R. S. Lane. Dewaxing lubricating oils with a mixture of butyl alcohol and acetone.
- U. S. 1,732,371, Oct. 22, 1929. M. Luther and K. Pieroh. Extracting resins from petroleum residues with methyl formate.
- U. S. 1,738,070, Dec. 3, 1929. P. Jodeck. Heating to expel sulfur dioxide from oils treated with liquid sulfur dioxide.
- U. S. 1,758,595, May 13, 1930. G. Cataneo. Apparatus for treating oils with liquid sulfur dioxide.
- U. S. 1,766,281, June 24, 1930. G. Cataneo and P. Jodeck. Apparatus for treating oils with liquid sulfur dioxide.
- U. S. 1,770,052, July 8, 1930. V. Voorhees. Using finely divided ice as filter aid for separating wax from the oil by filtration at low temperatures.
- U. S. 1,776,309, Sept. 23, 1930. F. M. Clark. Removing sludge-forming constituents from oils with glycerine.
- U. S. 1,776,550, Sept. 23, 1930. F. M. Clark and A. T. Harding. Similar to U. S. 1,776,309.
- U. S. 1,779,287, Oct. 21, 1930. J. K. Pfaff, K. Böttger, and A. Sieweke. Separating wax from oils by means of naphthalene.
- U. S. 1,781,420-1, Nov. 11, 1930. T. A. Werkenthin. Refining heavy petroleum oils with alcohol.
- U. S. 1,786,493, Dec. 30, 1930. E. W. Isom and E. B. Phillips. Refining vis-

- cons oils with adsorbents by heating to a temperature below cracking, and filtering.
- U. S. 1,788,569, Jan. 13, 1931. S. W. Ferris. Separation of naphthene hydrocarbons from paraffin hydrocarbons in a viscous oil by extraction with nitrobenzene.
- U. S. 1,789,026, Jan. 13, 1931. F. W. Sullivan, Jr. Lowering of cold test of lubricating oils by addition of zinc or magnesium salts of acidic products derived from oxidation of paraffin.
- U. S. 1,789,510, Jan. 20, 1931. J. C. Black. Recovery of sulfur dioxide in the Edeleanu process.
- U. S. 1,791,941, Feb. 10, 1931. K. T. Steik. Treating oils with a liquid mixture of sulfur dioxide and sulfur trioxide.
- U. S. 1,798,968, Mar. 31, 1931. F. M. Clark and A. T. Harding. Removing impurities from used insulating and lubricating oils with tricresyl phosphate.
- U. S. 1,802,942, Apr. 28, 1931. F. X. Govers. Dewaxing lubricating oils with acetone.
- U. S. 1,805,953, May 19, 1931. E. B. Auerbach. Treatment of lubricating oils with liquid carbon dioxide.
- U. S. 1,809,777, June 9, 1931. L. Edeleanu. Dewaxing lubricating oils by treating with liquid sulfur dioxide and filtering at low temperatures.
- U. S. 1,816,294, July 28, 1931. D. E. Pierce. Removing gum- and color-forming constituents from gasoline by contacting their vapors with a mineral oil substantially free from such substances.
- U. S. 1,820,295, Aug. 25, 1931. H. T. Bennett. Lowering the pour point of crude petroleum by adding aluminum stearate.
- U. S. 1,820,645, Aug. 25, 1931. H. T. Bennett. Dewaxing mineral oils by diluting with petroleum naphtha and biphenyl and chilling.
- U. S. 1,824,521, Sept. 22, 1931. T. A. Werkenthin. Recovering by vacuum distillation alcohol which has been used in extracting lubricating oils.
- U. S. 1,825,533, Sept. 29, 1931. A. Loebl. Separation of paraffin from mixed-base residuums by distillation after adding to the residuum the Edeleanu extract from coal tar.
- U. S. 1,825,762, Oct. 6, 1931. R. de M. Taveau. Extraction of lubricating oils with isopropyl alcohol.
- U. S. 1,826,392, Oct. 6, 1931. R. A. Dunham. Using Edeleanu extract or the oil recovered from acid sludge for dissolving rubber latex.
- U. S. 1,837,279, Dec. 22, 1931. W. J. McGill. Addition of about 5% or less of zinc or magnesium hydroxystearates to lower the cold test of lubricating oils.
- U. S. 1,838,029, Dec. 22, 1931. F. W. Isles. Apparatus for countercurrent treatment of petroleum oils with water, or various solutions of chemicals.
- U. S. 1,840,287, Jan. 5, 1932. F. Hofmann and C. Wulff. Extracting oil from carbonaceous residues from destructive distillation with liquid sulfur dioxide.
- U. S. 1,840,765, Jan. 12, 1932. G. Cattaneo, L. Edeleanu, W. Hess, P. Jodeck, and I. Rosenberg. Treatment of hydrocarbon oils with liquid sulfur dioxide.
- U. S. 1,847,600, Mar. 1, 1932. R. A. Dunham. The use of Edeleanu extract for reclaiming rubber.
- U. S. 1,847,601-6, Mar. 1, 1932. R. A. Dunham. The use of Edeleanu extract as a plasticizing material for rubber.
- U. S. 1,848,636, Mar. 8, 1932. C. J. Livingstone. Dewaxing with solvents, one of which is a poor wax solvent, such as ethylene dichloride, and the other a good wax solvent, such as benzene.
- U. S. 1,864,911, June 28, 1932. P. Jodeck. Apparatus for extracting oils with liquid sulfur dioxide.
- U. S. 1,868,333, July 19, 1932. J. C. Morrell and G. Egloff. Distillates containing sulfur and unsaturated hydrocarbons are treated with liquid sulfur dioxide. The separated saturated hydrocarbons are refined with sulfuric acid for removing the sulfur constituents and recombined with the unsaturated hydrocarbons.
- U. S. 1,871,172, Aug. 9, 1932. G. D. Graves. Wax is separated from foots oil by cooling the oil below its pour point, agitating to form a mushy suspension of wax and oil, and filtering.

- U. S. 1,871,694, Aug. 16, 1932. H. K. Ihrig. Crude gasoline is treated with liquid sulfur dioxide to separate the aromatic hydrocarbons.
- U. S. 1,874,946, Aug. 30, 1932. S. W. Ferris. Lubricating oils are extracted with phenyl acetate.
- U. S. 1,874,947, Aug. 30, 1932. S. W. Ferris. Lubricating oils are extracted with methyl or allyl thiocyanates.
- U. S. 1,885,524, Nov. 1, 1932. A. Lazar. Lubricating oil fractions are extracted with liquid sulfur dioxide, and the undissolved portion is decolorized by distilling in contact with an adsorbent clay.
- U. S. 1,893,138, Jan. 3, 1933. W. W. Gary. Refining petroleum oils with a mixture of liquid sulfur dioxide and liquid carbon dioxide.
- U. S. 1,895,195, Jan. 24, 1933. H. Limburg. Oil constituents insoluble in liquid sulfur dioxide are sulfonated at elevated temperatures to produce water-soluble sulfonic acids, the calcium salts of which are soluble in water and in calcium chloride solutions.
- U. S. 1,908,646, May 9, 1933. I. Rosenberg. Treatment of light petroleum distillates with liquid sulfur dioxide.
- U. S. 1,910,050, May 23, 1933. M. Pier, E. Anthes, and A. Eisenhut. Cracked materials boiling above the gasoline range are extracted with liquid sulfur dioxide, ammonia, or methyl alcohol, and the fraction poor in hydrogen is subjected to a destructive hydrogenation to obtain a non-detonating fuel.
- U. S. 1,910,341, May 23, 1933. P. Jodeck. Separation of sulfur dioxide from oils treated with liquid sulfur dioxide.
- U. S. 1,913,658, June 13, 1933. G. Cattaneo. Recovery of sulfur dioxide after extracting oils with liquid sulfur dioxide.
- U. S. 1,917,736, July 11, 1933. E. Saegbarth. Recovery of sulfur dioxide used for liquid phase extractions.
- U. S. 1,923,021, Aug. 15, 1933. W. P. Gee. Reconditioning filter-aids used in oil dewaxing by washing with hydrocarbon solvents.
- U. S. 1,925,525, Sept. 5, 1933. W. Dietrich and M. Harder. Oxygenated compounds obtained by oxidizing waxes or lubricating oils are separated by extraction with liquid sulfur dioxide containing an aliphatic alcohol or an aliphatic acid.
- U. S. 1,927,057, Sept. 19, 1933. J. A. Anderson. Oils are dewaxed by diluting with naphtha, chilling to separate part of the wax, adding a low boiling point wax to the mixture, and further chilling and filtering.
- U. S. 1,937,518, Dec. 5, 1933. L. M. Henderson, S. W. Ferris, and H. C. Cowles, Jr. Preparation of oil-free waxes.
- U. S. 1,941,251, Dec. 26, 1933. R. F. Davis. Cracked products are refined with liquid sulfur dioxide in the presence of tin tetrachloride, mercuric chloride, aluminum chloride, tin tetrabromide, iron trichloride, titanium tetrachloride, or zinc chloride.
- U. S. 1,941,809, Jan. 2, 1934. S. W. Ferris. Mixture of oil and wax is extracted with nitrobenzene, and the wax separated from the undissolved portion of the oil.
- U. S. 1,942,636, Jan. 9, 1934. H. T. Bennett and L. G. Story. Aluminum stearate is added to lubricating oil to reduce its pour point.
- U. S. 1,955,859, Apr. 24, 1934. R. T. Osborn and R. Craig. Sulfonic acids are obtained by treating sulfur dioxide extracts with sulfuric acid.
- U. S. 1,966,624, July 17, 1934. R. T. Haslam. Lubricating oils are produced by phenol extraction of residues obtained in the destructive hydrogenation of oils.
- U. S. 1,967,099, July 17, 1934. R. C. Osterstrom and C. R. Wagner. Dewaxing is facilitated by adding to the oil a synthetic oil produced by polymerizing cracked unsaturated hydrocarbons with aluminum chloride.
- U. S. 1,974,398, Sept. 18, 1934. E. Ellsberg. Shock-chilling of oils in dewaxing.
- U. S. 1,978,361, Oct. 23, 1934. G. A. Beiswenger. Dewaxing and deasphalting lubricating oils with pentane or light hydrocarbons.
- U. S. 1,979,232, Oct. 30, 1934. I. Rosenberg. Recovery of sulfur dioxide in the liquid sulfur dioxide extraction process.
- U. S. 1,982,120, Nov. 27, 1934. J. C. D.

- Oosterhout. Sulfur compounds are removed from phenols recovered from petroleum by passing their vapors through weathered lead sludge.
- U. S. 1,982,513, Nov. 27, 1934. W. Grote and P. Obergfell. Continuous refining of oils with liquid sulfur dioxide.
- U. S. 1,985,613, Dec. 25, 1934. G. McIntyre and E. G. Ulbricht. Cracked distillates are stabilized by washing them with ethylene glycol.
- U. S. 1,991,389, Feb. 19, 1935. L. M. Henderson, S. W. Ferris, and H. C. Cowles, Jr. Sweatability of crude scale wax is improved by adding needle type of wax to the crude scale wax.
- U. S. 1,994,485, Mar. 19, 1935. I. M. Perkins and F. B. Hobart. Sweating crude scale wax by passing it counter-currently to a solution of sodium silicate.
- U. S. 2,000,244, May 7, 1935. D. R. Merrill and A. L. Blount. Petroleum oils are extracted with selective solvents, such as liquid sulfur dioxide, and then treated with sodium carbonate solution. Naphthenic acids and phenols are recovered by acidifying the wash sodium carbonate solution with sulfuric acid.
- U. S. 2,093,538, Sept. 21, 1937. H. T. Bennett and D. B. Mapes. Oils are dewaxed in solution with 2-ethyl-hexanol.
- U. S. 2,003,667, June 4, 1935. E. F. Pevere. Dewaxing oils by diluting with a mixture of cyclohexanone and benzene, chilling, and filtering out the precipitated wax.
- U. S. 2,007,114, July 2, 1935. R. K. Stratford. Oil is treated with phenol, the undissolved portion is cracked and then refined with clay.
- U. S. 2,013,663, Sept. 10, 1935. W. M. Malisoff. Sulfur is removed from light petroleum distillates by extraction with a polyhydric alcohol or its ether.
- U. S. 2,022,259, Nov. 26, 1935. J. V. Starr. Apparatus for countercurrent extraction of petroleum oils with selective solvents.
- U. S. 2,024,117, Dec. 10, 1935. W. M. Stratford. Refining gasolines with a mixture of furfural and water.
- U. S. 2,026,651, Jan. 7, 1936. D. E. Payne. Apparatus for dewaxing oil with propane.
- U. S. 2,028,121, Jan. 14, 1936. O. P. Cottrell. Production of high octane number fuels by a combination of cracking and liquid sulfur dioxide extraction.
- U. S. 2,028,349, Jan. 21, 1936. M. Pier and F. Christmann. Lubricating oil of low pour test and high viscosity index is prepared by adding to the mineral oil a small quantity of wax, a viscosity index improver and a pour point depressant.
- U. S. 2,031,117-8, Feb. 18, 1936. D. R. Merrill and P. Subkow. Dewaxing lubricating oils with liquid propane.
- U. S. 2,033,942, Mar. 17, 1936. S. S. Kurtz, Jr. Extracting lubricating oils with dibutyl sulfone.
- U. S. 2,034,495, Mar. 17, 1936. F. W. Sullivan, Jr. Cracked distillates are extracted with a mixture of liquid sulfur dioxide and carbon dioxide to separate the high octane number constituents.
- U. S. 2,035,584, Mar. 31, 1936. J. R. Bailey. Separation of nitrogen bases from oils by converting them into chlorides and extracting the chlorides with chloroform.
- U. S. 2,044,996, June 23, 1936. W. J. Podbielniak. Apparatus for countercurrent refining of oils by pumping them through a passage of increasing diameter which is rotated to force the denser material outwardly.
- U. S. 2,045,696, June 30, 1936. S. E. Campbell. Cracked distillate is extracted with liquid sulfur dioxide; the extract is refined with sulfuric acid and alkalis and then blended with the raffinate.
- U. S. 2,046,951, July 7, 1936. E. B. Hjerpe and W. A. Gruse. Lubricating oils are extracted with butyl or isopropyl lactate or isopropyl glycolate.
- U. S. 2,047,380, July 14, 1936. W. B. McCluer and M. R. Fenske. Lubricating oils are extracted with methyl salicylate.
- U. S. 2,047,755, July 14, 1936. W. H. Volck. Unsaturated constituents are removed from distillates by treating with acetone containing small quantities of ammonia.
- U. S. 2,048,522, July 21, 1936. O. F. Simons. Extraction of gasoline with liquid sulfur dioxide to obtain constitu-

- ents of high antidetonating properties.
- U. S. 2,053,457, Sept. 8, 1936. H. T. Bennett and J. L. Burkitt. Oils are separated from Chlorex by means of sulfuric acid.
- U. S. 2,057,923, Oct. 20, 1936. E. J. Slater. Cylinder stocks are dewaxed by diluting with naphtha, chilling, and centrifuging, and then refined with sulfuric acid and clay.
- U. S. 2,063,597, Dec. 8, 1936. O. Fitz-Simons and F. C. Croxton. Cracked distillates are extracted with a mixture of liquid sulfur dioxide and pyridine to separate the constituents of high antidetonating properties.
- U. S. 2,068,126, Jan. 19, 1937. O. Fitz-Simons and R. A. Jack. Refining gasoline with ethyl alcohol.
- U. S. 2,069,172, Jan. 26, 1937. C. C. Miller. Extraction of cracked liquefied gases with cresylic acid.
- U. S. 2,069,329, Feb. 2, 1937. P. J. Roelfsema. Desulfurization of oils by fractionating them in the presence of acetone, nitrobenzene, or sulfur dioxide.
- U. S. 2,071,590, Feb. 23, 1937. E. W. Thiele and F. W. Scheineman. Extraction of naphtha with liquid sulfur dioxide.
- U. S. 2,073,517, Mar. 9, 1937. O. Fitz-Simons and W. H. Bahlke. Separation of antidetonating fractions by treating gasoline with liquid sulfur dioxide and propane.
- U. S. 2,078,992, May 4, 1937. D. B. Banks and P. D. Barton. Dewaxing oils with propane.
- U. S. 2,079,782, May 11, 1937. P. J. Wizevich. Pour point of lubricating oils is reduced and the oils are stabilized by addition of dimethylnaphthalene and an aliphatic polymer.
- U. S. 2,079,885, May 11, 1937. V. Voorhees. Solvent-refining of lubricating oils with chlorophenol or chloroaniline.
- U. S. 2,079,886, May 11, 1937. V. Voorhees. Refining lubricating oils with propane and phenol.
- U. S. 2,079,911, May 11, 1937. P. C. Keith, Jr., and H. O. Forrest. Deasphalting oils with propane, followed by extraction with selective solvents.
- U. S. 2,080,088, May 11, 1937. F. R. Moser. Lowering pour point of lubricating oils by adding a small portion of a furfural, a phenol, or a nitrobenzene extract which has been refined with propane.
- U. S. 2,080,222, May 11, 1937. H. L. Duffy. Dewaxing oils with solvents containing acetone.
- U. S. 2,080,415, May 18, 1937. S. W. Ferris. Extracting lubricating oils with quinoline.
- U. S. 2,081,174, May 25, 1937. C. Ellis. Deasphalting and dewaxing oils with propane and phenol.
- U. S. 2,081,287, May 25, 1937. B. G. Aldridge. Dewaxing oils by agitating the oil-solvent mixture with carbon dioxide or propane while chilling.
- U. S. 2,081,296, May 25, 1937. E. W. Gard. Filtering chilled oil-wax slurries while under the pressure induced by the solvent propane.
- U. S. 2,081,297, May 25, 1937. R. J. Garofalo and C. E. Swift. Oil is conditioned for dewaxing by treatment with clay containing asphaltic constituents, such as that recovered from crank-case oil.
- U. S. 2,081,310, May 25, 1937. P. Subkow. Refining kerosene with liquid propane and liquid sulfur dioxide.
- U. S. 2,081,403, May 25, 1937. H. O. Lindgren. Precipitating wax in oils in naphtha solution, followed by centrifuging in the presence of a heavier solvent, such as ethylene dichloride.
- U. S. 2,081,494, May 25, 1937. D. R. Merrill. Refining lubricating oils with Chlorex.
- U. S. 2,081,495, May 25, 1937. D. R. Merrill. Refining lubricating oils with selective solvents.
- U. S. 2,081,497, May 25, 1937. D. R. Merrill. Extracting oils with liquid sulfur dioxide and propane.
- U. S. 2,081,518, May 25, 1937. M. L. Wade. Pour point of lubricating oils is lowered by adding a mixture of montan wax and a reaction product of cracked pitch with a chlorinated aliphatic hydrocarbon.
- U. S. 2,081,519, May 25, 1937. M. L. Wade. Before dewaxing with propane, the oils are mixed with a condensation product of an aromatic hydrocarbon with a chlorinated aliphatic hydrocarbon and carnauba wax, montan wax, or similar substance.

- U. S. 2,081,524, May 25, 1937. C. D. Barnes. Extracting lubricating oils with a mixture of Chlorex and acetamide.
- U. S. 2,081,719, May 25, 1937. W. J. D. van Dijck. Refining oils with selective solvents.
- U. S. 2,081,720, May 25, 1937. W. J. D. van Dijck. Countercurrent gradient in solvent extraction of oils.
- U. S. 2,081,721, May 25, 1937. W. J. D. van Dijck and A. W. J. Mayer. Recovering oil from solvent extracts by reducing their solvent content.
- U. S. 2,081,731, May 25, 1937. U. B. Bray. Refining oils with propane.
- U. S. 2,081,732, May 25, 1937. U. B. Bray and D. E. Carr. Dewaxing lubricating oils with propane.
- U. S. 2,081,733, May 25, 1937. U. B. Bray and C. E. Swift. Deasphalting oils with propane.
- U. S. 2,081,734, May 25, 1937. U. B. Bray. Refining oils with propane.
- U. S. 2,081,884, May 25, 1937. E. N. Roberts. Recovery of Chlorex from oils.
- U. S. 2,083,247, June 8, 1937. K. Taylor and B. H. Shoemaker. Extracting lubricating oils with chlorex or nitrobenzene in contact with aluminum chloride.
- U. S. 2,083,250, June 8, 1937. V. Voorhees. Extracting lubricating oils with a mixture of liquid sulfur dioxide and dimethyl ether.
- U. S. 2,083,511, June 8, 1937. M. H. Tuttle. Apparatus for refining lubricating oils with solvents.
- U. S. 2,083,700, June 15, 1937. H. O. Forrest and L. Van Horn. Dewaxing oils with propane.
- U. S. 2,083,893, June 15, 1937. L. A. Clarke. Refining lubricating oils with anisidine or phenetidine.
- U. S. 2,084,342, June 22, 1937. W. F. Houghton. Refining lubricating oils with nitrobenzene.
- U. S. 2,084,352, June 22, 1937. L. Libberthson. Lowering pour point of lubricating oils with volatilized oils extracted with butyl alcohol.
- U. S. 2,084,471, June 22, 1937. J. M. Whiteley, Jr. Solvent refining with phenol, furfural, or nitrobenzene in the presence of benzene.
- U. S. 2,084,512, June 22, 1937. C. C. Swoope and M. M. Sadlon. Low pour point oils are prepared by blending two oils of different viscosities and a pour point inhibitor.
- U. S. 2,085,518, June 29, 1937. W. J. D. van Dijck. Extraction of lubricating oils with furfural in the presence of a little naphthalene.
- U. S. 2,085,519, June 29, 1937. C. G. Verver. Dewaxing with ethyl alcohol and benzol in contact with a little of a reaction product of alcohol and aniline or phenol.
- U. S. 2,085,521, June 29, 1937. A. P. Anderson and C. M. Kellogg. Apparatus for continuous dewaxing with propane.
- U. S. 2,085,546, June 29, 1937. P. J. Roelfsema. Refining with selective solvents.
- U. S. 2,086,168, July 6, 1937. D. R. Merrill. Extracting lubricating oils with selective solvents.
- U. S. 2,086,484, July 6, 1937. C. C. Towne. Extracting lubricating oils with resorcinol monomethyl ether.
- U. S. 2,086,487, July 6, 1937. W. H. Bahlke, F. W. Sullivan, Jr., and R. E. Wilson. Refining lubricating oils with propane.
- U. S. 2,086,666, July 13, 1937. H. F. Fisher. Separating wax from oil by electrical precipitation.
- U. S. 2,087,473, July 20, 1937. F. X. Govers. Lubricating oils are extracted with methyl-, ethyl-, propyl-, butyl-, or amyl-levulinate.
- U. S. 2,087,682, July 20, 1937. G. H. B. Davis and C. C. Swoope. Pour point inhibitor is prepared by reacting halogenated hydrocarbons with aluminum chloride.
- U. S. 2,088,441, July 27, 1937. P. L. Salzberg. Extraction of lubricating oils with furfurylamine.
- U. S. 2,088,898, Aug. 3, 1937. F. W. Breth. Pour point depressant prepared by voltolizing the oil.
- U. S. 2,089,984, Aug. 17, 1937. G. W. Ritter. Dewaxing with ethylene dichloride and naphtha.
- U. S. 2,091,400, Aug. 31, 1937. F. W. Sullivan, Jr., W. H. Bahlke, A. B. Brown, and F. F. Diwocky. Lubricating oils are extracted with chlorinated acetal.

- U. S. 2,081,524, May 25, 1937. C. D. Barnes. Extracting lubricating oils with a mixture of Chlorex and acetamide.
- U. S. 2,081,719, May 25, 1937. W. J. D. van Dijck. Refining oils with selective solvents.
- U. S. 2,081,720, May 25, 1937. W. J. D. van Dijck. Countercurrent gradient in solvent extraction of oils.
- U. S. 2,081,721, May 25, 1937. W. J. D. van Dijck and A. W. J. Mayer. Recovering oil from solvent extracts by reducing their solvent content.
- U. S. 2,081,731, May 25, 1937. U. B. Bray. Refining oils with propane.
- U. S. 2,081,732, May 25, 1937. U. B. Bray and D. E. Carr. Dewaxing lubricating oils with propane.
- U. S. 2,081,733, May 25, 1937. U. B. Bray and C. E. Swift. Deasphalting oils with propane.
- U. S. 2,081,734, May 25, 1937. U. B. Bray. Refining oils with propane.
- U. S. 2,081,884, May 25, 1937. E. N. Roberts. Recovery of Chlorex from oils.
- U. S. 2,083,247, June 8, 1937. K. Taylor and B. H. Shoemaker. Extracting lubricating oils with chlorex or nitrobenzene in contact with aluminum chloride.
- U. S. 2,083,250, June 8, 1937. V. Voorhees. Extracting lubricating oils with a mixture of liquid sulfur dioxide and dimethyl ether.
- U. S. 2,083,511, June 8, 1937. M. H. Tuttle. Apparatus for refining lubricating oils with solvents.
- U. S. 2,083,700, June 15, 1937. H. O. Forrest and L. Van Horn. Dewaxing oils with propane.
- U. S. 2,083,893, June 15, 1937. L. A. Clarke. Refining lubricating oils with anisidine or phenetidine.
- U. S. 2,084,342, June 22, 1937. W. F. Houghton. Refining lubricating oils with nitrobenzene.
- U. S. 2,084,352, June 22, 1937. L. Lieberthson. Lowering pour point of lubricating oils with volatilized oils extracted with butyl alcohol.
- U. S. 2,084,471, June 22, 1937. J. M. Whiteley, Jr. Solvent refining with phenol, furfural, or nitrobenzene in the presence of benzene.
- U. S. 2,084,512, June 22, 1937. C. C. Swoope and M. M. Sadlon. Low pour point oils are prepared by blending two oils of different viscosities and a pour point inhibitor.
- U. S. 2,085,518, June 29, 1937. W. J. D. van Dijck. Extraction of lubricating oils with furfural in the presence of a little naphthalene.
- U. S. 2,085,519, June 29, 1937. C. G. Verver. Dewaxing with ethyl alcohol and benzol in contact with a little of a reaction product of alcohol and aniline or phenol.
- U. S. 2,085,521, June 29, 1937. A. P. Anderson and C. M. Kellogg. Apparatus for continuous dewaxing with propane.
- U. S. 2,085,546, June 29, 1937. P. J. Roelfsema. Refining with selective solvents.
- U. S. 2,086,168, July 6, 1937. D. R. Merrill. Extracting lubricating oils with selective solvents.
- U. S. 2,086,484, July 6, 1937. C. C. Towne. Extracting lubricating oils with resorcinol monomethyl ether.
- U. S. 2,086,487, July 6, 1937. W. H. Bahlke, F. W. Sullivan, Jr., and R. E. Wilson. Refining lubricating oils with propane.
- U. S. 2,086,666, July 13, 1937. H. F. Fisher. Separating wax from oil by electrical precipitation.
- U. S. 2,087,473, July 20, 1937. F. X. Govers. Lubricating oils are extracted with methyl-, ethyl-, propyl-, butyl-, or amyl-levulinate.
- U. S. 2,087,682, July 20, 1937. G. H. B. Davis and C. C. Swoope. Pour point inhibitor is prepared by reacting halogenated hydrocarbons with aluminum chloride.
- U. S. 2,088,441, July 27, 1937. P. L. Salzberg. Extraction of lubricating oils with furfurylamine.
- U. S. 2,088,898, Aug. 3, 1937. F. W. Breth. Pour point depressant prepared by voltolizing the oil.
- U. S. 2,089,984, Aug. 17, 1937. G. W. Ritter. Dewaxing with ethylene dichloride and naphtha.
- U. S. 2,091,400, Aug. 31, 1937. F. W. Sullivan, Jr., W. H. Bahlke, A. B. Brown, and F. F. Diwocky. Lubricating oils are extracted with chlorinated acetal.

- U. S. 2,091,624, Aug. 31, 1937. J. C. Black and M. L. Chappell. Dewaxing oils with propane, and treating them with sulfuric acid before the wax is separated from the oil.
- U. S. 2,092,199, Sept. 7, 1937. M. H. Arveson. Refining lubricating oils with a mixture of phenol and liquid ammonia.
- U. S. 2,092,739, Sept. 7, 1937. W. J. D. van Dijk. Chloroquinoline and nitropyridine are used as selective solvents for extracting lubricating oils.
- U. S. 2,092,748, Sept. 14, 1937. E. R. Birkhimer. Phenylmethanol is used for extracting lubricating oils.
- U. S. 2,094,802, Oct. 5, 1937. W. B. McCluer and M. R. Fenske. Extracting lubricating oils with paraldehyde.
- U. S. 2,095,972, Oct. 19, 1937. W. F. Faragher. Extraction of lubricating oils with solvents in two stages by adjusting the composition of the extract phase from the first stage through the addition of paraffinic compounds.
- U. S. 2,096,314, Oct. 19, 1937. D. B. Banks and P. D. Barton. Removing filter cake with a gas blast.
- U. S. 2,096,725, Oct. 26, 1937. C. E. Andrews and M. R. Fenske. Extraction of lubricating oils with methylaniline.
- U. S. 2,096,871, Oct. 26, 1937. G. T. Atkins, Jr. Phenol is recovered from its constant-boiling mixture with water by contacting the mixed vapors with the oil to be charged to the phenol solvent refining unit.
- U. S. 2,096,950, Oct. 26, 1937. R. E. Wilson. Removing dichloroethyl ether or acetone from oils.
- U. S. 2,097,728, Nov. 2, 1937. P. C. Keith, Jr. Dewaxing with propane.
- U. S. 2,097,999, Nov. 2, 1937. E. M. Dons and D. B. Mapes. Dewaxing with propane.
- U. S. 2,098,007, Nov. 2, 1937. E. M. Dons and D. B. Mapes. Dewaxing with propane.
- U. S. 2,098,545, Nov. 9, 1937. B. Hoppper and K. Kingman. Dewaxing with propane.
- U. S. 2,098,766, Nov. 9, 1937. C. F. Tears. Washing percolation filters with liquefied hydrocarbon gases under pressure.
- U. S. 2,099,190, Nov. 16, 1937. C. D. Barnes and M. T. Flaxman. Improving dewaxing characteristics of lubricating oils by addition of wool grease, lanolin, or other substances containing cholesterol.
- U. S. 2,100,070, Nov. 23, 1937. A. D. David. Ductile wax of black color is produced by oxidizing petrolatum with air.
- U. S. 2,100,099, Nov. 23, 1937. C. C. Buchler and J. M. Page, Jr. Dewaxing lubricating oils in solution in Chlorex.
- U. S. 2,100,429, Nov. 30, 1937. U. B. Bray. Extracting lubricating oils with a mixture of liquid sulfur dioxide and benzene, followed by extracting with propane.
- U. S. 2,100,707, Nov. 30, 1937. S. S. Bhatnagar. Extracting hydrocarbon oils with acetic acid.
- U. S. 2,100,915, Nov. 30, 1937. E. F. Pevere. Improving dewaxing characteristics of lubricating oils by addition of glycerol tristearate.
- U. S. 2,100,916, Nov. 30, 1937. E. F. Pevere and C. G. Ludeman. Improving dewaxing characteristics of lubricating oils by adding a hydroxystearic acid esterified with stearic acid.
- U. S. 2,101,308, Dec. 7, 1937. U. B. Bray and C. E. Swift. Lubricating oil is diluted with naphtha, the precipitated asphalt is removed, and the oil-naphtha solution is extracted with liquid sulfur dioxide, furfural, or other selective solvent.
- U. S. 2,101,497, Dec. 7, 1937. J. H. Grahame. Extracting lubricating oils with furfural and beta-trichloroethane.
- U. S. 2,101,643, Dec. 7, 1937. E. F. Engelke. Extraction of lubricating oils from residuum with a mixture of amyl, butyl, and isopropyl alcohols.
- U. S. 2,102,334, Dec. 14, 1937. E. Petty. Dewaxing with propane.
- U. S. 2,102,828. P. D. Barton and D. B. Banks. Apparatus for filtering wax from the chilled solution of lubricating oil in liquid propane.
- U. S. 2,103,504, Dec. 28, 1937. J. M. Whiteley and H. G. Vesterdal. Refining crude petroleum with liquid propane or ethane.
- U. S. 2,104,379, Jan. 4, 1938. D. Stryker and J. H. Grahame. Lubricating oils

- are prepared by deasphalting with propane, extracting the oil-propane solution with furfural, and dewaxing after addition of another dewaxing solvent.
- U. S. 2,104,401, Jan. 4, 1938. E. V. Murphree and E. D. Reeves. Recovery by distillation of solvents used in extracting lubricating oils.
- U. S. 2,106,234, Jan. 25, 1938. U. B. Bray. Lubricating oils are extracted with chloroaniline and dewaxed after addition of liquid propane.
- U. S. 2,106,247, Jan. 25, 1938. A. H. Gleason. Pour point of lubricating oils is lowered by adding a reaction product of methyl oleate or oleic acid with naphthalene and similar hydrocarbons.
- U. S. 2,106,960, Feb. 1, 1938. M. Pier and A. Eisenhut. Ceresin is refined with propane and then extracted with phenol or nitrobenzene.
- U. S. 2,106,964, Feb. 1, 1938. A. A. Wells. Centrifugal dewaxing with carbon tetrachloride or ethylene dichloride as solvent.
- U. S. 2,107,064, Feb. 1, 1938. H. van der Waerden. Dewaxing oils with a mixture of acetone and tetrahydronaphthalene.
- U. S. 2,107,137, Feb. 1, 1938. C. E. Adams, F. W. Sullivan, Jr., and J. A. Anderson. Dewaxing oils with a mixture of acetone and cracked naphtha.
- U. S. 2,107,291, Feb. 8, 1938. S. W. Ferris. Extraction of lubricating oils with mixtures of nitrobenzene and resorcinol or pyrogallol.
- U. S. 2,107,429, Feb. 8, 1938. B. W. Story and V. A. Kalichevsky. Extraction of lubricating oils with a mixture of aniline and benzol.
- U. S. 2,107,770, Feb. 8, 1938. M. L. Wade. Electrical precipitation of wax is facilitated by the addition of cresol, nitrobenzene, or similar compounds to the oil.
- U. S. 2,107,771, Feb. 8, 1938. M. L. Wade. Electrical precipitation of wax from oil is facilitated by the addition of montanic, carnaubic, melissic, cerotic, or stearic acids to the oil.
- U. S. 2,107,772, Feb. 8, 1938. M. L. Wade. Electrical precipitation of wax is facilitated by addition of montan wax, carnauba wax or beeswax.
- U. S. 2,107,807, Feb. 8, 1938. H. Suida, H. Pöll, and A. Nowak. Lubricating stocks are extracted with cresol saturated with water, and the raffinate is re-extracted with an anhydrous solvent.
- U. S. 2,108,629, Feb. 15, 1938. W. R. van Wijk. Extracting lubricating oil stocks with solvents after they are chilled and at least partially solidified.
- U. S. 2,108,636, Feb. 15, 1938. H. V. Atwell. Preparation of fuel oil by extracting cracking tar with propane.
- U. S. 2,109,125, Feb. 22, 1938. B. G. Aldridge and B. Hopper. Dewaxing by electrical precipitation of wax.
- U. S. 2,109,130-1, Feb. 22, 1938. H. F. Fisher. Dewaxing oils by electrical precipitation of the wax.
- U. S. 2,109,157, Feb. 22, 1938. S. Tijmstra. The oil is distilled in the presence of a selective solvent to separate paraffinic hydrocarbons from naphthenic hydrocarbons, and the residue is extracted with additional quantities of solvent for further separation.
- U. S. 2,109,350, Feb. 22, 1938. L. Dillon. Dewaxing oils by electrical precipitation of wax.
- U. S. 2,109,476, Mar. 1, 1938. S. W. Ferris and E. R. Birkhimer. Extracting lubricating oils with a mixture of nitrobenzene and carbital.
- U. S. 2,109,895, Mar. 1, 1938. J. A. Anderson. Refining lubricating oils with selective solvents, followed by distillation to avoid treatment with a large quantity of adsorbent.
- U. S. 2,110,311, Mar. 8, 1938. M. E. Spaght. Extracting lubricating oils with liquid sulfur dioxide followed by extraction with acetic acid.
- U. S. 2,110,627, Mar. 8, 1938. E. B. Hjerpe and W. A. Gruse. Dewaxing oil with a mixture of benzene and acetone, followed by solvent extraction of the filtered solution with liquid sulfur dioxide.
- U. S. 2,110,845, Mar. 8, 1938. J. M. Whiteley and G. A. Beiswenger. Countercurrent refining of oils with liquid propane.
- U. S. 2,111,360, Mar. 15, 1938. F. C. Cutting. Oil is refined with solvents, and the extracted portion is subjected to distillation to remove some of the solvent and to obtain further recovery of oil.

- U. S. 2,111,760, Mar. 22, 1938. G. D. Graves. A condensation product of octadecanediol is added to lubricating oils to lower the pour point.
- U. S. 2,111,822, Mar. 22, 1938. F. W. Sullivan, Jr. Recovery of phenol in solvent extraction of lubricating oils.
- U. S. 2,111,864, Mar. 22, 1938. A. L. Lyman. Extraction of lubricating oils with a mixture of aniline and benzol.
- U. S. 2,111,957, Mar. 22, 1938. D. B. Banks. Depropanizing mixtures of wax and propane.
- U. S. 2,111,968, Mar. 22, 1938. S. W. Ferris. Lubricating oils are extracted with chloroaniline or chloronitrobenzene.
- U. S. 2,113,008, Apr. 5, 1938. C. F. Tears. Dewaxing heavy lubricating oils with propane, followed by contacting the solution with adsorbents at elevated temperature and under pressure.
- U. S. 2,113,179, Apr. 5, 1938. W. B. Kay. Preparation of a pour point depressant from chlorinated wax and naphthalene by employing liquid propane as a solvent.
- U. S. 2,114,467, Apr. 19, 1938. S. C. Fulton and J. M. Whiteley. Separation of wax is improved by addition of a product obtained by heating cracking tar with aluminum chloride.
- U. S. 2,114,812, Apr. 19, 1938. O. M. Reiff and D. E. Badertscher. A compound obtained by alkylating paraffin wax is acylated and used as a pour point depressant.
- U. S. 2,114,524, Apr. 19, 1938. H. Egli. Procedure for solvent extraction of distillate oil with liquid sulfur dioxide and a hydrocarbon diluent.
- U. S. 2,115,003, Apr. 26, 1938. G. A. Beiswenger. Separation of propane from oil in solvent extractions.
- U. S. 2,115,401, Apr. 26, 1938. W. H. Shiffler and J. Q. Cope. Separation of phenol from oil in the phenol refining of oils.
- U. S. 2,115,704, May 3, 1938. E. R. Brownscombe. Extracting lubricating oils with nitrobenzene mixed with acetic, phthalic, or maleic anhydride.
- U. S. 2,115,823, May 3, 1938. F. L. Miller and C. Winning. Cellulose stearate is used as a pour point depressant.
- U. S. 2,115,843, May 3, 1938. O. H. Dawson. Preparation of sulfonic acids from the sulfur dioxide extracts.
- U. S. 2,115,846, May 3, 1938. P. K. Frolich. Deasphalting and dewaxing with propane.
- U. S. 2,115,960, May 3, 1938. H. F. Lindeke. Oils are distilled. The resulting fractions are separately extracted with selective solvents, and recombined.
- U. S. 2,116,144, May 3, 1938. H. R. Dickinson. Dewaxing lubricating oils by atomizing them into a mixture of butyl alcohol and diethylcarbinol.
- U. S. 2,116,188, May 3, 1938. D. Churchill, Jr. Extracting crude paraffin at elevated temperatures with liquid propane and hexane.
- U. S. 2,116,428, May 3, 1938. M. R. Fenske. Refining mineral oils with solvents.
- U. S. 2,116,540, May 10, 1938. O. L. Roberts. Refining oils with nitrobenzene in countercurrent manner and maintaining the same temperature in the non-adjacent extraction stages but a different temperature in intermediate stage.
- U. S. 2,116,772, May 10, 1938. E. B. Tucker and E. W. Thiele. Separation of propane from the asphalt precipitated from oil.
- U. S. 2,118,766, May 24, 1938. J. Moos and H. Ramser. Oils are dewaxed with a mixture of ethanesulfonyl chloride and benzol.
- U. S. 2,118,915, May 31, 1938. R. J. Butz and R. C. Cantelo. Pour point of lubricating oils is reduced by addition of acids produced in the oxidation of paraffin wax.
- U. S. 2,119,718, June 7, 1938. E. F. Pevere. A glycerol tri-ester of stearic acid is used as a pour point depressant.
- U. S. 2,119,733, June 7, 1938. U. B. Bray. Dewaxing and deasphalting with liquid propane.
- U. S. 2,119,759, June 7, 1938. K. L. Walin. Separation of asphalt from a precipitated mixture of asphalt and wax by first removing the residual oil with selective solvents and then heating the mixture to liquefy the wax, which is then separated from the still solid asphalt.
- U. S. 2,119,871, June 7, 1938. J. M. Whiteley. Deasphalting lubricating oils

- with mixtures of liquefied propane and ethane.
- U. S. 2,119,938, June 7, 1938. C. D. Barnes and M. T. Flaxman. Oxidized lanolin or wool grease is added to lubricating oils to facilitate dewaxing with liquid propane.
- U. S. 2,119,940, June 7, 1938. D. E. Carr and M. L. Wade. Dewaxing of lubricating oils is facilitated by the addition of oxidized wax.
- U. S. 2,120,209, June 7, 1938. U. B. Bray. Refining lubricating oils with liquid sulfur dioxide.
- U. S. 2,120,810, June 14, 1938. G. L. Parkhurst. Extracting lubricating oils with a mixture of phenol and liquid sulfur dioxide.
- U. S. 2,121,323, June 21, 1938. R. E. Manley, B. Y. McCarty, and H. H. Gross. Solvent refining with furfural in the presence of a gelatinous material.
- U. S. 2,121,325, June 21, 1938. D. R. Merrill. Method of applying selective solvents to oils.
- U. S. 2,121,326, June 21, 1938. E. F. Pevere. Reaction product of phenanthrene with aluminum chloride is used as a pour point depressant.
- U. S. 2,121,517, June 21, 1938. D. G. Brandt. Deasphalting oils with propane.
- U. S. 2,122,019, June 28, 1938. C. E. Adams and F. W. Scheinman. Dewaxing lubricating oils with propane.
- U. S. 2,122,457, July 5, 1938. E. M. Dons, O. G. Mauro, and D. B. Mapes. Apparatus for refining lubricating oils with solvents.
- U. S. 2,123,205, July 12, 1938. O. L. Roberts. Nitrothiophene is used as solvent for extracting lubricating oils.
- U. S. 2,123,833, July 12, 1938. E. C. Knowles. Solvent dewaxing with the aid of wax modifiers.
- U. S. 2,123,982, July 19, 1938. E. R. Wiles. High melting point waxes are made by distilling the lubricating oil stock, dewaxing the residue with ethylene dichloride, and washing the precipitated wax with warm ethylene chloride.
- U. S. 2,124,531, July 26, 1938. F. R. Moser. Dewaxing of mineral oils in solution in cracked residuum or in polymerized liquid sulfur dioxide extracts, and cooling.
- U. S. 2,124,606, July 26, 1938. J. A. Buchel and R. N. J. Saal. Solvent refining of hydrocarbon oils with a mixture of acetone and benzol.
- U. S. 2,126,055, Aug. 9, 1938. J. V. Starr. Dewaxing with a mixture of acetone or isopropyl alcohol and a hydrogenated solvent extract.
- U. S. 2,126,493, Aug. 9, 1938. D. S. McKittrick and H. J. Henriques. Solvent dewaxing of lubricating oils.
- U. S. 2,127,325, Aug. 16, 1938. L. A. Clarke. Recovery of aniline from oils with the use of carbon dioxide.
- U. S. 2,127,708, Aug. 23, 1938. V. Voorhees. Dewaxing lubricating oils with propane.
- U. S. 2,128,029, Aug. 23, 1938. W. B. Hendrey. Recovery of phenol from oils with ammonia.
- U. S. 2,128,109, Aug. 23, 1938. P. J. Gaylor. A condensation product from chlorinated paraffin and an ether is used as a pour point depressant.
- U. S. 2,128,885, Aug. 30, 1938. J. W. Poole. Solvent refining of lubricating oils.
- U. S. 2,128,958, Sept. 6, 1938. M. Mueller-Cunradi and R. Uloth. Extracting lubricating oils with nitrobenzene and acetonitrile.
- U. S. 2,129,282, Sept. 6, 1938. J. M. Page, Jr. Solvent refining of lubricating oils with a mixture of Chlorex and propylene.
- U. S. 2,129,616, Sept. 6, 1938. W. Grote and A. Hoppe. Solvent refining and dewaxing with mixtures of liquid sulfur dioxide and benzene.
- U. S. 2,129,752, Sept. 13, 1938. J. M. Whiteley. A product obtained by chlorinating and then dechlorinating paraffin wax is used to improve the separation of the wax in dewaxing oils with chlorinated solvents.
- U. S. 2,130,126, Sept. 13, 1938. S. W. Ferris. Solvent refining of lubricating oils with cresols.
- U. S. 2,130,147, Sept. 13, 1938. O. H. Milmore. Extracting lubricating oils with solvents.
- U. S. 2,131,422, Sept. 27, 1938. A. P. Anderson. Refining lubricating oils in solution of low-boiling hydrocarbons by extraction with cresylic acid.

- U. S. 2,131,999, Oct. 4, 1938. L. A. Clarke. Nitro- or amino-biphenyl is used for extracting motor fuels to improve the antiknock characteristics.
- U. S. 2,132,108, Oct. 4, 1938. E. C. Herthel. Dewaxing with high-boiling alkyl esters and a low-boiling hydrocarbon solvent.
- U. S. 2,132,150, Oct. 4, 1938. M. R. Fenske. Apparatus for extracting oils with solvents.
- U. S. 2,132,151, Oct. 4, 1938. M. R. Fenske and W. B. McCluer. Apparatus for extracting oils with solvents.
- U. S. 2,132,350, Oct. 4, 1938. L. A. Clarke. Resorcinol monoacetate is used for extracting hydrocarbon oils.
- U. S. 2,132,355, Oct. 4, 1938. E. C. Knowles. Dewaxing with the aid of aluminum stearate or montan wax, which improves the crystallization of the wax.
- U. S. 2,132,359, Oct. 4, 1938. B. Y. McCarty. Solvent extraction of lubricating oils with furfural.
- U. S. 2,133,618, Oct. 18, 1938. B. Hopper and K. Kingman. Dewaxing with liquid propane.
- U. S. 2,133,691, Oct. 18, 1938. A. W. Francis. Extracting lubricating oils with pyridine containing the chloride, bromide, iodide, or acetate of lithium.
- U. S. 2,134,241, Oct. 25, 1938. K. Süsselbeck. Refining hydrocarbon distillates in the vapor phase with phenol or cresol.
- U. S. 2,134,336, Oct. 25, 1938. E. C. Knowles. Dewaxing in the presence of crystal modifying agents.
- U. S. 2,134,337, Oct. 25, 1938. E. C. Knowles. Dewaxing in pentane solution.
- U. S. 2,135,044, Nov. 1, 1938. J. H. Bartlett and A. H. Gleason. Preparation of a pour point depressant by condensing chlorinated wax with naphthalene.
- U. S. 2,135,363, Nov. 1, 1938. R. de M. Taveau, L. A. Clarke, and R. E. Manley. Solvent refining of lubricating oils with isopropyl or butyl alcohol and furfural.
- U. S. 2,135,468, Nov. 1, 1938. G. H. Morey. Hydrocarbon oils are extracted with 3-nitro-4-heptanol.
- U. S. 2,135,922, Nov. 8, 1938. E. Terres, J. Moos, and H. Ramser. Lubricating oils are extracted with sulfur hexafluoride.
- U. S. 2,136,767, Nov. 15, 1938. E. Terres, J. Moos, and H. Ramser. Lubricating oils are extracted with ortho-fluoroanisole.
- U. S. 2,136,885. F. R. Moser and M. C. Tuyn. Nitroaniline is added to lubricating oils to improve their film strength.
- U. S. 2,137,206, Nov. 15, 1938. F. X. Govers. Extracting lubricating oils with methylfurfural.
- U. S. 2,137,207, Nov. 15, 1938. J. H. Grahame and W. L. Douthett. Dewaxing and deasphalting oils with liquid propane.
- U. S. 2,137,208, Nov. 15, 1938. H. H. Gross and W. Kiersted, Jr. Dewaxing with mixtures of methyl-ethyl ketone and benzene.
- U. S. 2,137,209, Nov. 15, 1938. E. C. Knowles. Dewaxing with mixtures of methyl-ethyl ketone and benzene in the presence of wax modifiers.
- U. S. 2,137,218, Nov. 15, 1938. F. X. Govers. Dewaxing and solvent extraction with a mixture of methylene chloride and liquid sulfur dioxide.
- U. S. 2,137,499, Nov. 22, 1938. R. Z. Moravec. Extraction of lubricating oils with tertiary-butyl alcohol and methyl-ethyl ketone.
- U. S. 2,137,549, Nov. 22, 1938. P. Subkow. Dewaxing by leaching congealed or solidified oil with chlorinated solvents, such as trichloroethylene.
- U. S. 2,138,166, Nov. 29, 1938. A. W. Hixson and R. Miller. Hydrocarbon oils are refined by extraction with chloronitroethane.
- U. S. 2,138,771, Nov. 29, 1938. E. F. Pevere. Mannitan tetrastearate is added to a lubricating oil to improve its viscosity index and lower the pour point.
- U. S. 2,138,772, Nov. 29, 1938. E. Saegbarth. Para-chloro-phenol is used for extracting lubricating oils.
- U. S. 2,138,773, Nov. 29, 1938. E. Terres, J. Moos, and E. Saegbarth. Benzal acetone is used for extracting dewaxed lubricating oils.
- U. S. 2,138,809, Nov. 29, 1938. O. M. Reiff and D. E. Badertscher. Prepa-

- ration of pour point depressants by condensing phenol or similar materials with a chlorinated paraffin and acylating the resulting product.
- U. S. 2,138,832, Dec. 6, 1938. A. B. Brown and F. F. Diwoky. Extracting lubricating oils with a mixture of Chlorex and isopropyl ether.
- U. S. 2,138,868, Dec. 6, 1938. L. Libberthson. Pour point of lubricating oils is reduced by adding about 5% by volume of a waxy lubricating oil treated with ultraviolet light.
- U. S. 2,139,000, Dec. 6, 1938. C. A. Cohen. Amyl nitrite or tritoyl phosphate is used for the extraction of cracked distillates.
- U. S. 2,139,240, Dec. 6, 1938. E. G. McFarland. Removing solvents that are partially miscible with water from oils by distillation with the aid of steam.
- U. S. 2,139,392, Dec. 6, 1938. S. Tijmstra. Method for extracting lubricating oils with solvents.
- U. S. 2,139,773, Dec. 13, 1938. R. Rosen and C. A. Cohen. Dimethyl phthalate is used for refining cracked products.
- U. S. 2,139,871, Dec. 13, 1938. R. R. Wilson, E. K. Brown, and F. L. White. Apparatus for treating oils with Chlorex.
- U. S. 2,140,485, Dec. 13, 1938. E. Terres, E. Sagebarth, J. Moos, and H. Ramser. Lubricating oils are refined by dewaxing with dichlorodifluoromethane and adding a secondary solvent to separate the low viscosity index constituents.
- U. S. 2,141,085, Dec. 20, 1938. E. B. IJjerpe and W. A. Gruse. Mixtures of ethylene dichloride and liquid sulfur dioxide are used for extracting lubricating oils.
- U. S. 2,141,143, Dec. 20, 1938. E. Terres, J. Moos, and E. Sagebarth. Ethylene tetrabromide is used for extracting lubricating oils.
- U. S. 2,141,257, Dec. 27, 1938. E. W. Thiele and B. Ginsberg. Filtering of propane deasphalted oils is facilitated by addition of a small quantity of a reduced pressure tar.
- U. S. 2,141,361, Dec. 27, 1938. S. Pilat and M. Godlewicz. Dewaxing lubricating oils, followed by washing the precipitated wax with selective solvents.
- U. S. 2,141,511, Dec. 27, 1938. C. C. Buchler and S. H. Diggs. Mixtures of Chlorex and alkylene glycol are used for extracting lubricating oils.
- U. S. 2,141,601, Dec. 27, 1938. C. E. Francis and B. S. Greensfelder. Penta-stearylglucose is added to lubricating oils to inhibit the separation of visible wax.
- U. S. 2,141,605, Dec. 27, 1938. W. B. Hendrey and L. W. Cook. Tetrahydrofurfuryl acetate and acetic acid mixtures are used to extract lubricating oils.
- U. S. 2,142,219-20, Jan. 3, 1939. E. M. Steffen. The pour point of lubricating oil is lowered by adding the reaction product of rubber with aluminum chloride.
- U. S. 2,142,525, Jan. 3, 1939. H. D. Noll. Extraction of lubricating oils with cresylic acid and propane.
- U. S. 2,142,939, Jan. 3, 1939. A. W. Francis. Pyridine containing calcium nitrate is used for extracting lubricating oils.
- U. S. 2,143,415, Jan. 10, 1939. A. W. Hixson and R. Miller. Orthomethoxybenzonitrile is used for extracting lubricating oils.
- U. S. 2,143,872, Jan. 17, 1939. H. O. Forrest and L. Van Horn. Apparatus for extracting oils with propane.
- U. S. 2,143,882, Jan. 17, 1939. P. C. Keith, Jr., R. E. Wilson, and M. J. Livingston. Apparatus for refining oils with propane.
- U. S. 2,144,797, Jan. 24, 1939. E. M. Dons, O. G. Mauro, and D. B. Mapes. Apparatus for solvent extraction of oils.
- U. S. 2,145,185, Jan. 24, 1939. E. Terres, E. Sagebarth, and J. Moos. A glyceryl ester of propionic or butyric acid is used for extracting lubricating oils.
- U. S. 2,145,828-9, Jan. 31, 1939. L. A. Clarke and E. C. Knowles. Mixtures of chlorophenol and chloroacetic acid are used for extracting lubricating oils.
- U. S. 2,146,147, Feb. 7, 1939. P. C. Keith, Jr., and H. O. Forrest. Refining lubricating oils with liquid propane and selective solvents.
- U. S. 2,146,650, Feb. 7, 1939. O. S. Pokorny. Triphenyl phosphate is used for extracting lubricating oils.

- U. S. 2,146,679, Feb. 7, 1939. E. Koennemann and H. Ramser. Refining lubricating oils with liquid sulfur dioxide.
- U. S. 2,147,222, Feb. 14, 1939. J. P. Treub. Method for countercurrent dewaxing.
- U. S. 2,147,315, Feb. 14, 1939. M. Pier and F. Christmann. Oleyl alcohol treated with thionyl chloride is used as a pour point depressant.
- U. S. 2,147,545, Feb. 14, 1939. O. M. Reiff. Pour point of lubricating oils is improved by the addition of a condensation product of chlorinated ester wax with phenol, resorcinol, hydroxybiphenyl, benzyl phenol, or an aromatic ester.
- U. S. 2,147,546, Feb. 14, 1939. O. M. Reiff. Pour point of lubricating oils is reduced by adding to lubricating oils a product obtained by condensing chlorinated ester wax with an aromatic hydrocarbon and then with formaldehyde.
- U. S. 2,147,547, Feb. 14, 1939. O. M. Reiff and D. E. Badertscher. Pour point of lubricating oils is reduced by adding a product obtained by condensing an aromatic hydrocarbon with a chlorinated aliphatic hydrocarbon and acylating.
- U. S. 2,147,573, Feb. 14, 1939. L. W. Cook and C. C. Towne. A reaction product of rubber with tin or boron halide is added to oils to improve the filter rates when they are dewaxed with mixtures of methyl-ethyl ketone and benzene.
- U. S. 2,147,579, Feb. 14, 1939. E. C. Knowles. Dewaxing oils in the presence of wax modifiers.
- U. S. 2,147,786, Feb. 21, 1939. M. R. Fenske and W. B. McCluer. Apparatus for refining oils with solvents.
- U. S. 2,148,292, Feb. 21, 1939. C. E. Francis. Beeswax, spermaceti, bayberry wax, candelilla wax, carnauba wax, Chinese wax, cocoa wax, cottonseed wax, Japan wax, or montan wax are added to lubricating oils to prevent formation of a wax cloud.
- U. S. 2,148,710, Feb. 28, 1939. C. L. Read. An increase in yield of lubricating oil is obtained by adding to the solvent extract water, methyl alcohol, etc. and collecting the oil separated from the extract material.
- U. S. 2,148,716, Feb. 28, 1939. J. M. Whiteley and G. A. Beiswenger. Deasphalting oils with liquid propane.
- U. S. 2,149,322-3, Mar. 7, 1939. M. H. Tuttle. Refining lubricating oils with liquid propane and mixtures of selective solvents.
- U. S. 2,149,531, Mar. 7, 1939. W. B. McCluer and M. R. Fenske. Lubricating oils are dissolved in pyridine, from which they are precipitated in steps by the addition of methylcellosolve.
- U. S. 2,149,574, Mar. 7, 1939. A. B. Brown. Extraction of lubricating oils with cresylic acid and propane in a countercurrent tower.
- U. S. 2,149,752, Mar. 7, 1939. F. P. Vickery. Petroleum oils are extracted with mixtures of acetone and ethylene glycol.
- U. S. 2,150,156, Mar. 14, 1939. M. A. Dietrich. A halogenated castor oil reaction product with an aldehyde, alcohol, isocyanate, or isothiocyanate is used as a pour point depressant.
- U. S. 2,150,183, Mar. 14, 1939. W. A. Myers. Extracting lubricating oils with a mixture of nitrobenzene, nitrotoluene, and diethylene glycol ethyl ether.
- U. S. 2,150,334, Mar. 14, 1939. D. S. McKittrick and H. J. Henriques. Lubricating oils are dewaxed with a mixture of ethylene glycol methyl ether and secondary butyl alcohol.
- U. S. 2,150,501, Mar. 14, 1939. R. A. Halloran and A. L. Lyman. Viscous pitch obtained by heating sulfuric acid sludge from refining cracked distillates is used to facilitate dewaxing of lubricating oils.
- U. S. 2,150,547, Mar. 14, 1939. W. B. Hendrey and E. C. Knowles. Aluminum stearate or lead naphthenate is used to improve the filterability of wax distillates.
- U. S. 2,150,552, Mar. 14, 1939. E. C. Knowles. Montan wax is added to facilitate dewaxing of lubricating oils with solvents.
- U. S. 2,151,318, Mar. 21, 1939. L. Dillon and C. E. Swift. Acid is added to a waxy oil in order to facilitate the separation of the wax by electrodeposition.
- U. S. 2,151,529, Mar. 21, 1939. O. L.

- Roberts. Extraction of lubricating oils with nitrobenzene.
- U. S. 2,151,592, Mar. 21, 1939. S. W. Ferris. Extraction of lubricating oil with nitrobenzene.
- U. S. 2,151,619, Mar. 21, 1939. F. Schick. Extraction of paraffin wax with phenols, followed by sweating and by decolorization with activated carbon.
- U. S. 2,153,116, Apr. 4, 1939. E. Eichwald. Solvent extraction and distillation of lubricating oils.
- U. S. 2,153,353, Apr. 4, 1939. M. H. Tuttle. Refining lubricating oils with liquid propane and nitrobenzene.
- U. S. 2,153,507, Apr. 4, 1939. M. D. Mann, Jr. Countercurrent apparatus for solvent extraction of petroleum oils.
- U. S. 2,153,895, Apr. 11, 1939. D. S. McKittrick and H. J. Henriques. Dewaxing mineral oils with a mixture of isopropyl alcohol and 1,2-dichloroethane or dichloroethene.
- U. S. 2,154,189, Apr. 11, 1939. J. W. Weir. Pyridine is used for extracting lubricating oils in the presence of sodium hydroxide solution.
- U. S. 2,154,372, Apr. 11, 1939. E. A. Bosing. Lubricating oils are extracted with pyridine in the presence of potassium nitrite, potassium carbonate, or sodium acid sulfide solutions.
- U. S. 2,155,204, Apr. 18, 1939. C. F. Prutton. Halogenated petroleum oils and similar substances are treated with aluminum chloride to render them suitable for use as addition agents in lubricating oils.
- U. S. 2,155,644, Apr. 25, 1939. L. P. Evans. Extracting lubricating oils with furfural and hydrocarbon solvents.
- U. S. 2,155,645, Apr. 25, 1939. L. P. Evans and H. H. Gross. Dewaxing with selective solvents in contact with aluminum stearate.
- U. S. 2,157,134, May 9, 1939. B. H. Lincoln and A. Henriksen. A reaction product from the reaction of anhydrous aluminum chloride or chlorinated stearic acid and naphthalene is used to improve film strength of lubricating oils.
- U. S. 2,157,821, May 9, 1939. S. W. Ferris. Lubricating oils are extracted with nitrobenzene and naphtha.
- U. S. 2,158,358, May 16, 1939. L. P. Evans. Dewaxing of lubricating oils with benzene-acetone solutions in the presence of a little aluminum stearate.
- U. S. 2,158,360, May 16, 1939. F. X. Govers. Liquid sulfur dioxide and chlorinated benzene are used for solvent extraction and dewaxing of lubricating oils.
- U. S. 2,158,361, May 16, 1939. F. X. Govers. Liquid sulfur dioxide and ethyl ether or isopropyl ether are used for solvent extraction and dewaxing of lubricating oils.
- U. S. 2,158,370, May 16, 1939. E. C. Knowles. Dewaxing of lubricating oils with selective solvents in the presence of montan wax.
- U. S. 2,158,671, May 16, 1939. D. E. Carr and M. L. Wade. Oxidized wax is used to facilitate the dewaxing of lubricating oils.
- U. S. 2,158,672, May 16, 1939. D. E. Carr and M. L. Wade. Lubricating oils that tend to form haze in storage are slightly oxidized with air prior to dewaxing.
- U. S. 2,159,444, May 23, 1939. W. B. McCluer and M. R. Fenske. Methyl ethyl ketone is used for the solvent extraction of lubricating oils.
- U. S. 2,160,136, May 30, 1939. P. K. Frolich. Preparation of hydrocarbon solvents by extraction with liquid sulfur dioxide and destructive catalytic hydrogenation of the undissolved fractions.
- U. S. 2,160,573, May 30, 1939. B. S. Greensfelder and M. E. Spaght. Cyclic nitrogen bases obtained from cracked distillates are used as dewaxing solvents.
- U. S. 2,160,607, May 30, 1939. W. J. D. van Dijck. Thiophene aldehyde is used for solvent extraction of cracked distillates.
- U. S. 2,160,930, June 6, 1939. J. M. Whiteley and H. G. Vesterdal. Dewaxing hydrocarbon oils with liquefied hydrocarbon.
- U. S. 2,160,985, June 6, 1939. O. S. Pokorny. Dewaxing lubricating oils with aliphatic ketones.
- U. S. 2,161,567, June 6, 1939. W. P. Gee and M. Neuhaus. Method for refining lubricating oils with solvents.

- U. S. 2,161,572, June 6, 1939. W. B. Hendrey. Solvent refining and dewaxing lubricating oils with mixtures of para-chlorophenol and chloroform.
- U. S. 2,161,581, June 6, 1939. E. C. Knowles. Dewaxing oils with the aid of cellulose stearate and montan wax.
- U. S. 2,161,753. E. Terres, J. Moos, and E. Saegbarth. Dibromohydrin is used for extracting lubricating oils.
- U. S. 2,162,195, June 13, 1939. B. S. Greensfelder and M. E. Spaght. Oxidation of lubricating oils with air prior to the extraction with selective solvents.
- U. S. 2,162,682, June 13, 1939. E. Terres, J. Moos, and H. Ramser. Halogenated aliphatic hydrocarbons containing fluorine are used for selective solvent extraction of lubricating oils.
- U. S. 2,163,245, June 20, 1939. K. C. Laughlin. Solvent extracts are digested with sulfur, at a relatively high temperature, and then extracted with selective solvents.
- U. S. 2,163,564, June 20, 1939. E. Terres, E. Saegbarth, J. Moos, and H. Ramser. Dichloro-difluoromethane is used for deasphalting lubricating oils.
- U. S. 2,163,858, June 27, 1939. R. D. Snow. Extraction of lubricating oils with a mixture of liquid sulfur dioxide, olefins, and rosin oil.
- U. S. 2,164,013, June 27, 1939. V. N. Jenkins. Dewaxing lubricating oils by emulsifying with sodium hydroxide solutions and chilling.
- U. S. 2,164,193, June 27, 1939. D. S. McKittrick. Apparatus for refining lubricating oils with solvents.
- U. S. 2,164,391, July 4, 1939. E. M. Dons and D. B. Mapes. Mixture of isopropyl acetate and amyl acetate is used as a dewaxing solvent.
- U. S. 2,164,769, July 4, 1939. F. X. Govers. Dewaxing lubricating oils with a mixture of liquid sulfur dioxide and ortho-dichlorobenzene.
- U. S. 2,164,773, July 4, 1939. E. C. Knowles. Dewaxing lubricating oils with a mixture of benzene and acetone.
- U. S. 2,164,776, July 4, 1939. B. Y. McCarty. Dewaxing of lubricating oils is facilitated by the presence of a pitchy residue obtained from cracking still tar.
- U. S. 2,164,777, July 4, 1939. B. Y. McCarty and H. H. Gross. Method for extracting lubricating oils with solvents.
- U. S. 2,164,779, July 4, 1939. R. E. Manley. Dewaxing lubricating oils with a mixture of acetone and benzene.
- U. S. 2,164,780, July 4, 1939. E. F. Peverc. Tetranaphthyl is used to facilitate dewaxing of lubricating oils.
- U. S. 2,165,638, July 11, 1939. R. E. Manley. Dewaxing lubricating oils with furfural.
- U. S. 2,165,807, July 11, 1939. E. V. Murphree and E. D. Reeves. Dichloroethylene is used as a dewaxing solvent.
- U. S. 2,165,949, July 11, 1939. C. R. Wagner. Dewaxing with methyl ethyl ketone.
- U. S. 2,166,005, July 11, 1939. F. W. Hall. Dewaxing and deasphalting lubricating oils with liquid propane.
- U. S. 2,166,140, July 18, 1939. V. L. Hansley. Dimethyl formamide is used for solvent extraction of lubricating oils.
- U. S. 2,166,160, July 18, 1939. E. P. King. Solvent refining of lubricating oils with light hydrocarbons at elevated temperatures and high pressures.
- U. S. 2,167,340, July 25, 1939. E. W. Thiele. Dewaxing lubricating oils with liquefied propane.
- U. S. 2,167,632, Aug. 1, 1939. E. R. Brownscombe and S. W. Ferris. Recovery of nitrobenzene used in extracting lubricating oils.
- U. S. 2,167,730, Aug. 1, 1939. E. R. Smoley. Separation of furfural or phenol in the solvent refining processes.
- U. S. 2,167,970, Aug. 1, 1939. U. B. Bray. Dewaxing lubricating oils with mixtures of liquid sulfur dioxide and cyclopropylene.
- U. S. 2,168,140-3, Aug. 1, 1939. A. H. Schutte. Dewaxing oils by emulsifying them with water and centrifuging.
- U. S. 2,168,306, Aug. 1, 1939. A. H. Schutte. Dewaxing oils by agitating them with air and centrifuging the resulting foamy material.
- U. S. 2,168,330, Aug. 8, 1939. S. W. Ferris. Refining waxes by extraction with nitrobenzene.
- U. S. 2,168,570, Aug. 8, 1939. W. W.

- Kraft. Recovery of furfural or phenol in solvent extraction processes.
- U. S. 2,168,574, Aug. 8, 1939. D. B. Mapes and E. M. Dons. Mixtures of isopropyl acetate and amyl acetate are used for dewaxing oils.
- U. S. 2,168,875, Aug. 8, 1939. H. D. Noll. Method of extracting lubricating oils with paraffinic and naphthenic solvents.
- U. S. 2,169,218, Aug. 15, 1939. E. R. Brownscombe. Separating nitrobenzene from lubricating oils by extraction with dilute alcohol at elevated temperatures and under pressure.
- U. S. 2,170,508, Aug. 22, 1939. A. Schaafsma and J. M. Versteeg. Dewaxing lubricating oils with a mixture of trichloroethylene and Chlorex.
- U. S. 2,171,646, Sept. 5, 1939. A. B. Brown and F. F. Diwoky. Solvent extraction of lubricating oils with a mixture of chloroaniline and cresylic acid, or of chloroaniline and phenol, or of chlorophenol and cresylic acid.
- U. S. 2,172,320, Sept. 5, 1939. L. D. Jones. Centrifugal dewaxing with a mixture of naphtha and a chlorinated solvent.
- U. S. 2,173,915, Sept. 26, 1939. D. F. Reushaw. Refining lubricating oils with Chlorex.
- U. S. 2,174,174, Sept. 26, 1939. B. S. Greensfelder and M. E. Spaght. Cracked distillates are treated with a sulfo-acid and alkyl phenols.
- U. S. 2,174,246, Sept. 26, 1939. E. Lieber and M. M. Sadlon. Pour point depressants are prepared by condensing chlorinated paraffin with aromatic hydrocarbons.
- U. S. 2,174,938, Oct. 3, 1939. L. Dillon and C. E. Swift. Dewaxing lubricating oils by precipitating the wax under the influence of a high-voltage electrostatic field.
- U. S. 2,176,396, Oct. 17, 1939. M. R. Fenske and W. B. McCluer. Refining lubricating oils with selective solvents, followed by the recovery of additional quantities of oil from the extract phase by washing it with another solvent which is miscible with the first solvent.
- U. S. 2,176,429, Oct. 17, 1939. W. Kiersted, Jr. A tower for countercurrent extraction of lubricating oils with solvents.
- U. S. 2,176,432, Oct. 17, 1939. R. E. Manley. Dewaxing lubricating oils by centrifuging in the presence of furfural.
- U. S. 2,176,746, Oct. 17, 1939. O. S. Pokorny and G. W. Gurd. Lubricating oils are extracted with a mixture of beta-phenoxyethyl alcohol and triethylene glycol.
- U. S. 2,176,982-3, Oct. 24, 1939. G. Thayer. Centrifugal apparatus for extracting lubricating oils in naphtha solution with phenol.
- U. S. 2,177,183, Oct. 24, 1939. W. W. Kraft and M. A. Zimmerman. Recovery of cresylic acid or phenol by distillation.
- U. S. 2,177,923, Oct. 31, 1939. H. G. Berger, W. H. James, and D. E. Badertscher. Di- or tetra-wax phenol is reacted with ortho-phosphitobenzoyl chloride, and the resulting product is used to reduce the pour point and corrosiveness of lubricating oils.
- U. S. 2,178,078, Oct. 31, 1939. E. J. Martin. Dewaxing with a mixture of benzene or toluene, ethylene glycol monomethyl ether, and nitrobenzene.
- U. S. 2,178,321, Oct. 31, 1939. L. A. Clarke. Oils deficient in high viscosity index constituents are extracted with a mixture of phenol and chlorophenols which was previously used in extracting oils rich in high viscosity index constituents.
- U. S. 2,178,328, Oct. 31, 1939. L. G. Story. Heating waxy stocks with aluminum stearate, followed by chilling and filtering to dewax the oil.
- U. S. 2,178,506, Oct. 31, 1939. J. W. Weir. Dewaxing and solvent refining of lubricating oils with pyridine.
- U. S. 2,178,515, Oct. 31, 1939. E. Terres, J. Moos, and E. Saegbarth. Acetanilide is used in the solvent extraction of lubricating oils.
- U. S. 2,179,008, Nov. 7, 1939. S. E. Campbell. Apparatus for countercurrent refining of petroleum distillates with liquid reagents.
- U. S. 2,181,638, Nov. 28, 1939. L. W. Cook. Chromium soap of a higher fatty acid is used to facilitate dewaxing with a mixture of methyl-ethyl ketone and benzene.

- U. S. 2,184,838, Dec. 26, 1939. D. L. Hooker and C. M. Fabian. Apparatus for refining lubricating oils with propane and cresylic acid.
- U. S. 2,184,961, Dec. 26, 1939. A. Schlageter. Apparatus for counter-current extraction of lubricating oils with solvents.
- U. S. 2,185,291, Jan. 2, 1940. J. A. Buchel and R. N. J. Saal. Solvent extraction of lubricating oils with a mixture of furfural and chloroform.
- U. S. 2,185,311, Jan. 2, 1940. E. G. Ragatz and D. E. McFaddin. Recovery of sulfur dioxide and benzene from oils by distillation.

CHAPTER VIII.—DETONATION AND ANTIDETONANTS

- U. S. 929,503, July 27, 1909. G. B. Selden. Hydrogen peroxide is added to motor fuels to improve their performance.
- U. S. 1,131,880, Mar. 16, 1915. C. H. Warth. Preparation of motor fuel from kerosene and benzene.
- U. S. 1,749,244, Mar. 4, 1930. M. J. Fessler. Tetrahydronaphthalene is added to gasoline to reduce carbon formation in engines.
- U. S. 1,757,837, May 6, 1930. C. O. Johns. Preparation of motor fuel by blending gasoline with benzene and adding tetraethyl lead to the mixture.
- U. S. 1,757,838, May 6, 1930. C. O. Johns. Preparation of motor fuel by adding ethyl alcohol and tetraethyl lead to gasoline.
- U. S. 1,766,501, June 24, 1930. C. A. Buerk. Benzoyl peroxide, hydrogen peroxide, or naphthalene peroxide is added to gasoline to prevent formation of carbon deposits in engines.
- U. S. 1,787,419, Dec. 30, 1930. T. Midgley, Jr. Use of tetraethyl lead or various phenyl or alkyl compounds of lead, selenium, tellurium, tin, arsenic, or antimony for improving antidetonating properties of fuels.
- U. S. 1,798,593, Mar. 31, 1931. H. W. Daudt. Manufacture of tetracthyl lead.
- U. S. 1,800,822, Apr. 14, 1931. G. Egloff. Improving antiknock qualities of gasoline by blending it with pressure distillate obtained from cracking low temperature coal tar.
- U. S. 1,814,745, July 14, 1931. W. E. Elliott. Improving fuel oils by adding a composition made of naphthalene, nitrobenzene, paraffin oil, and aniline.
- U. S. 1,815,753, July 21, 1931. R. E. Wilson. Antidettonating fuel containing tetraethyl lead, ethylene bromide, nitrobenzene, xylene, kerosene, solvent naphtha, or similar components.
- U. S. 1,841,254, Jan. 12, 1932. R. R. Rosenbaum. Improving antiknock characteristics of motor fuels by adding esters of naphthenic acids (such as butyl ester of hydroxynaphthenic acid) or mercury compounds of naphthenic acids.
- U. S. 1,844,362, Feb. 9, 1932. H. K. Ihrig. Improvement in antiknock characteristics of gasoline by treating sulfur dioxide extract material with sulfuric acid, nitrating, reducing, treating with sodium hydroxide, and adding the portion containing aromatic amino derivatives to motor fuel.
- U. S. 1,848,063, Mar. 1, 1932. L. B. Kimball. Improving antiknock characteristics of motor fuel by adding aniline in the presence of butyl or ethyl alcohol to prevent the separation of aniline from the oil.
- U. S. 1,848,681, Mar. 8, 1932. V. Voorhees. Redistilling vapor-phase cracked gasoline which has lost its antiknock properties in storage to improve its antiknock characteristics.
- U. S. 1,868,053, July 19, 1932. A. J. Ducamp. Preignition in internal combustion engines is prevented by adding to the fuel a solution of mercury cyanide in glycerol.
- U. S. 1,868,102, July 19, 1932. L. M. Henderson and S. W. Ferris. Gasoline is fractionated, and fractions having high-antidettonating properties are segregated to produce a high antiknock fuel.
- U. S. 1,869,486, Aug. 2, 1932. V. Iantz. Triethylamine, benzylamine, or piperidine is added to a mixture of petroleum distillate and commercial alcohol to act as a blending agent without materially affecting the antiknock properties of fuels.

- U. S. 1,883,593, Oct. 18, 1932. R. Cross. Antiknock properties of gasoline are improved by the addition of cyanoforn.
- U. S. 1,885,190, Nov. 1, 1932. G. Egloff. Antiknock properties of gasoline are preserved in storage by addition of 2% of anthraquinone.
- U. S. 1,893,021, Jan. 3, 1933. P. S. Danner. Improvement of antidetonating characteristics of fuels by the addition of 0.1-1.0% of iron tetracarbonyl.
- U. S. 1,893,438, Jan. 3, 1933. A. Oberle. Purification and improvement of antidetonating characteristics of motor fuels by treatment with dilute water solutions of iodine or various iodine compounds.
- U. S. 1,894,661, Jan. 17, 1933. B. T. Brooks. Antiknock properties of motor fuels are improved by addition of polymers obtained by treatment of a petroleum fraction consisting mainly of butadiene and butene with sulfuric acid of 60-80% strength.
- U. S. 1,895,081, Jan. 24, 1933. W. Miller, A. Henriksen, and P. Zurcher. Antiknock properties of motor fuels are improved by vapor-phase refining with fuller's earth.
- U. S. 1,903,255, Mar. 28, 1933. F. E. L. Busch. Antidetonating properties of motor fuels are improved by addition of para-cymene.
- U. S. 1,903,624, Apr. 11, 1933. R. T. Hurley. Antidetonating properties of motor fuels are improved by the addition of iron carbonyl and a "corrective agent" comprising tetraethyl lead.
- U. S. 1,906,724, May 2, 1933. L. Rosenstein and W. J. Hund. Antidetonating properties of motor fuels are improved by addition of *sym-p*-dimethylanilino-diselenide.
- U. S. 1,915,917, June 27, 1933. E. V. Bereslavsky. Antidetonating properties of motor fuels are improved by addition of amino-compounds of cymene.
- U. S. 1,920,766, Aug. 1, 1933. L. Rosenstein and W. J. Hund. Antidetonating properties are improved by addition of dicyanodiselenide or similar compounds of selenium or tellurium.
- U. S. 1,938,546, Dec. 5, 1933. F. W. Sullivan, Jr., and V. Voorhees. Antidetonating properties of gasoline are improved by adding organic lead compounds which are obtained by establishing a silent electric discharge in metallic lead and hydrocarbon materials.
- U. S. 1,938,547, Dec. 5, 1933. F. W. Sullivan, Jr., and F. F. Diwoky. Preparation of antidetonating addition agents by activating hydrocarbon materials with a high-tension arc and immediately contacting them with metallic lead.
- U. S. 1,940,096, Dec. 19, 1933. M. Mueller-Cunradi and W. Wilke. Antidetonating properties of motor fuels are improved by addition of iron carbonyl and an amine, such as aniline or its derivatives.
- U. S. 1,940,439-40, Dec. 19, 1933. G. Alleman. Antidetonating properties of motor fuels are improved by addition of organic lead, thallium, or nickel compounds containing a dimethyl group.
- U. S. 1,948,449, Feb. 20, 1934. L. Rosenstein. Antidetonating properties of gasolines are improved by the addition of an organic derivative of metallocyanic acid, such as tetraisopropyl ester of hydroferrocyanic acid.
- U. S. 1,949,948-9, Mar. 6, 1934. G. Alleman. Improving antidetonating properties of motor fuels by the addition of lead tetraalkyls.
- U. S. 1,951,780, Mar. 20, 1934. V. Voorhees. Antidetonating properties of motor fuels are improved by freezing out the least desirable hydrocarbon constituents.
- U. S. 1,954,865, Apr. 17, 1934. P. S. Danner. Antidetonating properties of motor fuels are improved by the addition of metallic carbonyls.
- U. S. 1,958,744, May 15, 1934. R. Cross. Antidetonating properties of motor fuels are improved by the addition of cyanamide, cyanic acid, cyanoanilide, dicyanodiamide, urea, or hydrazine.
- U. S. 1,973,320, Sept. 11, 1934. A. Pacyna. Antidetonating properties of motor fuels are improved by the addition of uranium and vanadium chlorides.
- U. S. 1,973,474, Sept. 11, 1934. G. Egloff and R. E. Schaad. Antidetonating properties of motor fuels are improved by the addition of substances produced by cracking of hydrocarbon gases in contact with ammonia.

- U. S. 1,973,475, Sept. 11, 1934. C. Ellis. Sept. 11, 1934. Antiknock motor fuel containing oxidized petroleum hydrocarbons.
- U. S. 1,974,167, Sept. 18, 1934. V. Voorhees. Fused sodium chloride is electrolyzed in the presence of lead to form chlorine and a lead-sodium alloy. The chlorine is reacted with gasoline to form chlorinated hydrocarbons in the gasoline, and the gasoline is then treated with the alloy to form hydrocarbon compounds of lead in the gasoline to improve the antidetonating characteristics.
- U. S. 1,980,097, Nov. 6, 1934. G. F. Ruddies. Antiknock and anticarbonizing properties of motor fuels are improved by the addition of butyl oxalate or butyl phthalate, colloidal graphite, vanadium or platinum chloride, and a chloral hydrate.
- U. S. 1,982,420, Nov. 27, 1934. J. F. P. de la Riboisière. Antidetonating properties of motor fuels are improved by the addition of aniline and alcohol or acetone.
- U. S. 1,989,113, Jan. 29, 1935. E. Rector. Detonation is inhibited by injecting lead vapors with the gasoline into the engine.
- U. S. 1,991,127, Feb. 12, 1935. R. de M. Taveau. Antidetonating properties of fuels are improved by the addition of a butyl compound of lithium.
- U. S. 1,991,333, Feb. 12, 1935. E. F. Pevere. Diphenyl ditelluride is added to gasoline to improve its antidetonating characteristics.
- U. S. 1,994,243, Mar. 12, 1935. G. Egloff and R. E. Schaad. Antidetonating properties are improved by heating aromatic hydrocarbons with ammonia in the presence of activated carbon and adding the resulting products to motor fuels.
- U. S. 1,997,159, Apr. 9, 1935. C. C. Towne. Antidetonating fuel is produced by contacting gasoline with selenium at high temperature and pressure.
- U. S. 1,997,480, Apr. 9, 1935. R. E. Burk and E. C. Hughes. Antidetonating properties of motor fuels are improved by oxidizing hydrocarbon oils with air.
- U. S. 2,000,410, May 7, 1935. J. C. Morrell and G. Egloff. Antidetonating properties of motor fuels are improved by treating cracked vapors with phenol and ammonia.
- U. S. 2,000,411, May 7, 1935. J. C. Morrell and G. Egloff. Antidetonating properties are improved by contacting hydrocarbon vapors with sulfonating agents and then with sodamide.
- U. S. 2,000,412, May 7, 1935. J. C. Morrell and G. Egloff. Antidetonating properties are improved by treating hydrocarbon vapors with chlorine in the presence of a catalyst and then contacting them with sodamide.
- U. S. 2,002,805, May 28, 1935. H. G. Webster. Antidetonating properties of motor fuels are improved by the addition of di-nickel carbonyl.
- U. S. 2,012,356, Aug. 27, 1935. S. Shapirio. Gasoline is halogenated and treated with a lead-sodium alloy to improve its antidetonating properties.
- U. S. 2,018,570, Oct. 22, 1935. P. Pötschke. Tetraethyl lead is added to gasoline in the form of solid pellets containing stearic acid.
- U. S. 2,021,088, Nov. 12, 1935. E. F. Pevere. Ethylenediamine is used for improving antidetonating properties of gasolines.
- U. S. 2,023,142, Dec. 3, 1935. N. Max. Salicylal-methyl (or allyl) amine containing copper or cobalt is added to improve the antidetonating properties of motor fuels.
- U. S. 2,023,372, Dec. 3, 1935. N. Max. A copper salt of hydroxymethylene camphor is added to improve antidetonating properties of motor fuels.
- U. S. 2,064,842, Dec. 22, 1936. C. D. Lowry, Jr., and F. J. Skowronski. High-boiling gasoline fractions of cracked paraffinic oil are treated with a solvent, such as liquid sulfur dioxide; the resulting raffinate is further cracked, and the gasoline portion thereof blended with the low-boiling portion of the material extracted by the liquid sulfur dioxide to give better octane values.
- U. S. 2,065,588, Dec. 29, 1936. D. A. Howes. Ethyl or amyl nitrite and benzyl bromide are used to improve ignition characteristics of diesel fuels.
- U. S. 2,067,331, Jan. 12, 1937. J. M. Michel. Antidetonating properties of

- gasolines are improved by the addition of tetraethyl lead and ammonium fluoride.
- U. S. 2,067,764, Jan. 12, 1937. V. Ipatieff. Antidetoning properties of gasoline of high aromatic content are improved by reacting the gasoline with an olefin-containing gas catalyzed by pyrophosphoric acid and an adsorbent, such as kieselguhr.
- U. S. 2,078,736, Apr. 27, 1937. H. B. J. Schurink. Improving antidetonating properties of gasoline by the addition of tertiary butyl alcohol containing 12-35% water.
- U. S. 2,081,357, May 25, 1937. V. Ipatieff. Antiknock properties are improved by alkylating gasoline with propylene.
- U. S. 2,087,582, July 20, 1937. H. G. Schneider. Butyl or amyl alcohol is added to gasoline to improve its lead susceptibility.
- U. S. 2,087,660, July 20, 1937. F. W. Sullivan, Jr. Gasoline is produced by cracking, and immediately contacted with metallic lead to improve its antidetonating properties.
- U. S. 2,088,997, Aug. 3, 1937. N. Max. Mercuric salt (about 0.2%) of cobalt carbonyl hydride is added to improve the antiknock properties of motor fuels.
- U. S. 2,093,008, Sept. 14, 1937. A. C. G. Egerton. Diethyl peroxide is added to diesel fuels to shorten the delay period in ignition.
- U. S. 2,094,907, Oct. 5, 1937. J. D. Segny. Hydrogenating cracked distillates to produce high-antiknock fuels.
- U. S. 2,096,769, Oct. 26, 1937. H. Tropsch. Improving antiknock properties of gasoline by contacting its vapors with an aluminum oxide catalyst for 2 to 20 seconds at 840-1200° F.
- U. S. 2,096,813, Oct. 26, 1937. V. Komarewsky. Antiknock properties of gasoline are improved by condensing the gasoline with aromatic hydrocarbons.
- U. S. 2,109,866, Mar. 1, 1938. F. R. Moser. Antiknock properties of motor fuels are improved by contacting with boron phosphate at elevated temperatures.
- U. S. 2,128,910, Sept. 6, 1938. J. E. Bludworth. Antidetoning motor fuel comprising gasoline and alcohol.
- U. S. 2,132,968, Oct. 11, 1938. W. B. B. Penniman. Improving the antidetonating properties of gasoline by oxidation with air.
- U. S. 2,134,625, Oct. 25, 1938. S. Shapirio. Improving the antidetonating properties of motor fuels by the addition of lead amide or lead hydrazide.
- U. S. 2,135,327, Nov. 1, 1938. V. Conquest. Improving the antidetonating properties of motor fuels by the addition of stearo- or palmito-nitrile.
- U. S. 2,137,080, Nov. 15, 1938. H. G. M. Fischer and C. E. Gustafson. Improved motor fuel is produced by adding to gasoline tetraethyl lead and alpha-naphthylamine or alpha-naphthol.
- U. S. 2,140,627, Dec. 20, 1938. J. W. Hocking. Iron pentacarbonyl with a peptizing agent comprising a fat and ammonium oleate or similar substances is used to improve antiknock properties of gasolines.
- U. S. 2,143,870, Jan. 17, 1939. C. Ellis. Antidetoning properties of gasoline are improved by the addition of diisopropyl acetal.
- U. S. 2,145,889, Feb. 7, 1939. C. F. Prutton and D. R. Frey. Iron or nickel carbonyl and di-glycol stearate are added to gasoline to improve its antidetonating properties.
- U. S. 2,148,138, Feb. 21, 1939. F. W. Sullivan, Jr. Antiknock compounds are produced by contacting cracked vapors with vapors of lead.
- U. S. 2,149,033, Feb. 28, 1939. W. A. Schulze and G. G. Oberfell. Tetraethyl lead and ammonia are added to improve the performance of motor fuels having an end point below that of kerosene.
- U. S. 2,149,221, Feb. 28, 1939. R. H. Lamping. Iron carbonyl and stearic or oleic acid are added to improve antidetonating properties of gasolines.
- U. S. 2,150,349, Mar. 14, 1939. A. J. van Peski and J. A. van Melsen. A large number of antiknock additives is specified.
- U. S. 2,157,224, May 9, 1939. C. R. Wagner. Improving antidetonating properties of gasolines by heating them with olefinic gases at 840-1100° F. and at 500-2000 lb. pressure.

- U. S. 2,160,249, May 30, 1939. H. E. Drennan. Gasoline vapors are contacted with gypsum in order to improve the antidetonating properties of the gasoline.
- U. S. 2,163,269, June 20, 1939. J. A. Chenicek. Cinnamic aldehyde is used to extract high antidetonating hydrocarbons from gasoline stock.
- U. S. 2,164,334, July 4, 1939. E. M. Marks. Motor fuel of high antidetonating properties is produced by chlorinating and then dechlorinating naphtha.
- U. S. 2,166,544, July 18, 1939. T. Cross, Jr. Octane rating of heavy naphtha is improved by passing its vapors over Marsil clay.
- U. S. 2,167,602, July 25, 1939. W. A. Schulze. Improving the antidetonating properties of gasolines by passing their vapors over bauxite.
- U. S. 2,178,403, Oct. 31, 1939. I. E. Muskat. Allyl alcohol or diallyl alcohol or diallyl ether is used to improve the antidetonating properties of gasolines.
- U. S. 2,184,956, Dec. 26, 1939. E. R. Gilliland and R. Rosen. Antidetonating properties of gasoline are improved by the addition of 10% or more of glycol ether, such as mono- or di-tertiary-butyl ether of ethylene glycol.
- CHAPTER IX.—INHIBITORS OF ATMOSPHERIC OXIDATION OF PETROLEUM PRODUCTS. ANTIOXYGENS.
- U. S. 1,768,910, July 1, 1930. H. K. Ihrig. Addition to lubricants of nitrogenous bases extracted from petroleum to prevent development of acidic substances.
- U. S. 1,856,186, May 3, 1932. F. Hofmann and M. Dunkel. About 0.1% of toluonitrile is added to a transformer or a lubricating oil to prevent sludge formation in service.
- U. S. 1,857,761, May 10, 1932. W. L. McCabe and B. Mead. Stability of turbine and transformer oils is improved by adding 0.01-1.0% of an alkyl compound of lead or tin, such as tetraethyl lead.
- U. S. 1,882,887, Oct. 18, 1932. J. C. Pope. Transformer and similar oils are rendered resistant to oxidation by addition of 0.07% of tetraethyl lead and heating to 212-302° F.
- U. S. 1,888,023, Nov. 15, 1932. C. E. Adams. Color of lubricating oils is stabilized by adding 0.05-1.0% of butyl-diethanolamine.
- U. S. 1,891,093, Dec. 13, 1932. J. Hyman. Catechol or various hydroxy- or amino-derivatives or benzene, ammonia, or ammonia derivatives are added to the motor fuel to prevent fading of dyes added to the fuel.
- U. S. 1,909,069, May 16, 1933. J. W. Orelup. Cracked gasoline is stabilized by addition of pyridine, picoline, or other nitrogen bases found in shale oil.
- U. S. 1,909,985, May 23, 1933. J. B. Rather, L. C. Beard, Jr., and O. M. Reiff. Stabilizing the color of light petroleum distillates by addition of 0.02% or less of brucine in butyl alcohol solution or similar alkaloids.
- U. S. 1,913,370, June 13, 1933. L. P. Chebotar. Oxidation inhibitors are formed in cracked distillates by adding a component for forming indophenol and then a peroxide which is required for indophenol formation.
- U. S. 1,922,103, Aug. 15, 1933. T. E. Layng and M. A. Youker. Improving insulating properties of transformer oils by addition of sodium ethylate.
- U. S. 1,930,248, Oct. 10, 1933. J. C. Morrell. Gasoline is stabilized with camphor, camphorophorone, or camphoric acid.
- U. S. 1,940,445, Dec. 19, 1933. W. S. Calcott and I. E. Lee. Cracked gasolines are stabilized by the addition of 0.002% or more of a polybutylamine or an amylamine. Di- and tri-ethanolamines are also suitable.
- U. S. 1,951,205-7, Mar. 13, 1934. J. B. Rather, O. M. Reiff, and L. C. Beard, Jr. Resorcinol is added to cracked distillates to lessen the discoloration in storage.
- U. S. 1,966,050, July 10, 1934. R. G. Sloane. Heptyl mercaptan is used for stabilizing white oils.
- U. S. 1,966,111, July 10, 1934. A. E. Becker and W. S. Davis. Pale lubricating oils are rendered resistant to oxidation by admixing them with white lubricating oil.

- U. S. 1,973,676, Sept. 11, 1934. V. Voorhees. Ethylene diamine is used to stabilize the color of petroleum oils.
- U. S. 1,988,299, Jan. 15, 1935. F. M. Clark. Phenyl-alpha-naphthylamine is used to prevent sludging of transformer oils.
- U. S. 1,988,300, Jan. 15, 1935. F. M. Clark. Sludging of transformer oils is prevented by addition of para-nitrochlorobenzene, ortho-nitronaphthalene, meta-dinitrobenzene, hydroxydinitrobenzene, ortho- or para-nitrophenol, para-nitrobromobenzene, nitrochlorophenol, or dinitrophenol.
- U. S. 1,992,014, Feb. 19, 1935. T. H. Rogers and R. E. Wilson. Color stability of cracked distillates is improved by addition of alpha-naphthylamine or alpha-naphthol, and discoloration is prevented by addition of tributylamine.
- U. S. 1,995,615, Mar. 26, 1935. A. O. Jaeger. Diethyl maleate or dibutyl phthalate is added to cracked gasoline to improve its stability.
- U. S. 2,000,105, May 7, 1935. B. W. Story and E. W. Fuller. Beta-naphthol and dibenzyl disulfide are used to stabilize transformer oils.
- U. S. 2,001,108, May 14, 1935. C. K. Parker. Lubricating and transformer oils are stabilized by addition of calcium, manganese, lead, zinc, aluminum, or cobalt naphthenate.
- U. S. 2,002,645, May 28, 1935. J. B. Rather, L. C. Beard, Jr., and O. M. Reiff. Urea is added to gasoline to prevent discoloration in storage.
- U. S. 2,003,158, May 28, 1935. W. A. Smith. The color of cracked gasoline is improved and rendered stable by addition of quinhydrone.
- U. S. 2,004,560, June 11, 1935. R. E. Wilson. Cracked distillates containing tetraethyl lead are stabilized by adding para-benzyl aminophenol.
- U. S. 2,009,118, July 23, 1935. J. C. Morrell. Prior to the addition of inhibitors, the cracked distillates are fractionated to remove constituents which adversely affect the inhibitor.
- U. S. 2,014,235, Sept. 10, 1935. C. D. Lowry, Jr. Cracked distillates are stabilized by the addition of unrefined corn oil.
- U. S. 2,014,924, Sept. 17, 1935. W. L. Benedict. Triamylamine is added to cracked distillates to prevent discoloration.
- U. S. 2,016,648, Oct. 8, 1935. J. W. Orelup. Cracked distillates are stabilized with 1,4-dihydroxyanthraquinone.
- U. S. 2,023,110, Dec. 3, 1935. R. E. Wilson. Pyrogallol, hydroquinone, catechol, or gallic acid is added to gasolines containing alpha-naphthol or similar gum-inhibitors to prevent discoloration in storage.
- U. S. 2,031,930, Feb. 25, 1936. H. E. Buc. Tert-butyl phenol is used for stabilizing highly refined oils.
- U. S. 2,034,283, Mar. 17, 1936. L. A. Clarke and H. Levin. Oleic, stearic, palmitic, or benzoic ester of pyrogallol or similar polyhydric phenol is used for stabilizing cracked distillates.
- U. S. 2,051,814, Aug. 25, 1936. W. L. Benedict. The color of gasoline is stabilized by the addition of sodium phenolate.
- U. S. 2,051,871, Aug. 25, 1936. C. D. Lowry, Jr. Hydroxyphenylazo-alpha-naphthol is added to gasoline to prevent discoloration in storage.
- U. S. 2,051,872, Aug. 25, 1936. C. D. Lowry, Jr. Phenylazocatechol is added to gasoline to prevent discoloration in storage.
- U. S. 2,051,873, Aug. 25, 1936. C. D. Lowry, Jr. Para-nitrophenylazopyrogallol is added to gasoline to prevent discoloration in storage.
- U. S. 2,052,860, Sept. 1, 1936. C. P. Wilson, Jr. Reaction products of para-amino-phenol and turpentine are used to stabilize cracked distillates.
- U. S. 2,054,276, Sept. 15, 1936. C. P. Wilson, Jr. Aromatic amines containing components of turpentine as substituted groups are used for stabilizing cracked distillates.
- U. S. 2,055,810, Sept. 29, 1936. T. W. Bartram. Cracked distillates are stabilized by the addition of primary aromatic amines.
- U. S. 2,061,111, Nov. 17, 1936. D. R. Stevens and W. A. Gruse. An antioxidant for cracked distillates is prepared by interacting the cracked distillate with phenol or cresylic acid in the presence of sulfuric acid.

- U. S. 2,069,294, Feb. 2, 1937. C. P. Wilson, Jr. Stabilizing cracked distillates with a reaction product of phenol and the cracked distillate in the presence of sulfuric acid.
- U. S. 2,076,524, Apr. 13, 1937. F. B. Behrens. Elimination of peroxides formed in gasoline in storage by treating with burned magnesite.
- U. S. 2,081,886, May 25, 1937. B. W. Story and E. W. Fuller. Stabilization of transformer and lubricating oils with dibenzyl disulfide.
- U. S. 2,085,045, June 29, 1937. R. Rosen. Hydroxyphenyl amyl sulfide is used to stabilize lubricating oils.
- U. S. 2,090,484, Aug. 17, 1937. I. I. Ostromislensky. Cracked distillates are stabilized by addition of 4-hydroxyphenyl-azo-(1-phenyl-3-methyl)-pyrazolone or similar substances.
- U. S. 2,097,162, Oct. 26, 1937. J. M. Musselman and H. P. Lankelma. Tetramethyldiaminophenylmethane is added to lubricating oils to improve their stability.
- U. S. 2,100,685, Nov. 30, 1937. G. S. Cavanaugh. Sludge-forming characteristics of lubricating oils are lessened by the addition of diethylene oxide.
- U. S. 2,101,241, Dec. 7, 1937. J. Cole. Stability of lubricating oils against oxidation is improved by adding a reaction product of chlorinated wax and oleic acid.
- U. S. 2,104,049, Jan. 4, 1938. J. C. Morrell. Preparation of oxidation inhibitors from phenols extracted from petroleum oils.
- U. S. 2,104,796, Jan. 11, 1938. M. A. Dietrich. Stability of lubricating oils against oxidation is improved by adding beta-dicyclohexylaminoethyl methacrylate or similar derivatives of acrylic acid.
- U. S. 2,108,386, Feb. 15, 1938. J. M. Musselman and E. B. McConnell. N-paratolylglycyl-1,2-dihydroxybenzene is used to prevent the autoxidation of lubricating oils.
- U. S. 2,108,954, Feb. 22, 1938. J. I. Wasson. Stability of lubricating oils against oxidation is improved by the addition of an aliphatic hydroxy-sulfide.
- U. S. 2,110,274, Mar. 8, 1938. L. A. Mikeska and J. B. Holtzclaw. Tri-acetoxxytriethanolamine is added to cracked distillates to improve their stability.
- U. S. 2,110,950, Mar. 15, 1938. R. E. Burk and H. P. Lankelma. A tetrahydroxybicyclospiroindane is added to improve the color stability of paraffin wax.
- U. S. 2,111,306, Mar. 15, 1938. T. W. Bartram. Cracked distillates are stabilized by the addition of a sulfurized diaryl arylenediamine.
- U. S. 2,111,307, Mar. 15, 1938. T. W. Bartram. Cracked distillates are stabilized by the addition of cyclohexylnaphthylamine.
- U. S. 2,113,150, Apr. 5, 1938. P. J. Wiezevich. An aliphatic primary hydroxylamine is used to improve the stability of lubricating oils.
- U. S. 2,113,810, Apr. 12, 1938. B. H. Lincoln and W. L. Steiner. A sulfurized mono- or dihydric ester of linoleic acid is used to improve oil stability.
- U. S. 2,113,811, Apr. 12, 1938. B. H. Lincoln and W. L. Steiner. Sulfurized methyl esters of organic acids are used to improve oil stability.
- U. S. 2,114,437, Apr. 19, 1938. H. G. Berger and E. M. Nygaard. Cyclohexyl substitution products of hydroquinone or pyrogallol are used to stabilize gasolines.
- U. S. 2,115,355, Apr. 26, 1938. P. J. Wiezevich. Condensed diphenyl oxide is added to lubricating oils to improve the Sligh oxidation test.
- U. S. 2,115,781, May 3, 1938. J. C. Morrell. Organic peroxides are removed from gasolines by refining with ferrous chloride or ferrous sulfate.
- U. S. 2,117,602, May 17, 1938. R. Bulkley. Stability of turbine oils is improved by addition of Chlorox extract which has been extracted with acetone and refined with sulfuric acid.
- U. S. 2,119,114, May 31, 1938. R. W. Richardson and J. J. Owen. Oxidation of lubricating oils is retarded by the addition of a product prepared by electrical treatment of a Coastal red oil, beta-naphthol, rapeseed oil, and cetyl alcohol.
- U. S. 2,123,083, July 5, 1938. L. G. Story. Cracked distillates are stabilized

- with alpha-naphthylamine and pyrogallol or hydroquinone.
- U. S. 2,123,457, July 12, 1938. R. E. Wilson. An alkyl amino-phenol is used to stabilize highly refined lubricating oils.
- U. S. 2,125,961, Aug. 9, 1938. B. H. Shoemaker and C. M. Loane. Zinc or aluminum butylate is used to improve the color stability of lubricating oils.
- U. S. 2,136,788, Nov. 15, 1938. M. Fairlie. Quinaldine is used to improve the stability of lubricating oils.
- U. S. 2,139,766, Dec. 13, 1938. L. A. Mikeska and C. A. Cohen. Stability of lubricating oils is improved with dialkyl diphenol sulfides.
- U. S. 2,147,572, Feb. 14, 1939. L. A. Clarke and J. R. Callaway. Cracked distillates are bleached with alpha-methylhydroxylamine and stabilized with diphenylthiourea.
- U. S. 2,150,079, Mar. 7, 1939. C. F. Pritton. Ortho-dichlorobenzene is used to improve the oxidation stability of lubricating oils.
- U. S. 2,150,400, Mar. 14, 1939. R. Rosen-Allyl or phenyl isocyanate or isothiocyanate is added to lubricating oils to improve their oxidation stability.
- U. S. 2,153,121, Apr. 4, 1939. J. M. Musselman. Stability of lubricating oils is improved by the addition of quinine, cinchonine, or cinchonidine.
- U. S. 2,155,678, Apr. 25, 1939. J. C. D. Oosterhout. Lecithin is used to stabilize gasolines containing tetraethyl lead.
- U. S. 2,156,158, Apr. 25, 1939. E. T. Olson and R. Katzen. Wood-tar distillates are used for inhibiting cracked distillates.
- U. S. 2,158,668, May 16, 1939. R. Rosen. Diamyl trisulfide and triphenyl tin iodide, or a similar compound of bismuth or antimony, are used to improve the oxidation stability of lubricating oils.
- U. S. 2,160,138, May 30, 1939. P. J. Gaylor. Mixtures of primary aliphatic hydroxy amines are used for stabilizing lubricating oils.
- U. S. 2,160,851, June 6, 1939. J. Faust. Alkyl ammonium dithiocarbamate is used as oxidation inhibitor in medicinal oils.
- U. S. 2,161,317, June 6, 1939. A. N. Sachanen and P. G. Waldo. An oxidation inhibitor is prepared by treating cracked petroleum vapors with sulfuric acid.
- U. S. 2,161,566, June 6, 1939. E. W. Fuller. Ethyl ester of ethyl xanthate is used to improve the oxidation stability of turbine and white oils.
- U. S. 2,161,585, June 6, 1939. R. C. Moran and E. W. Fuller. Dixanthylethyl ether is used for stabilizing lubricating oils against oxidation.
- U. S. 2,162,208, June 13, 1939. R. C. Moran, W. H. James, and E. W. Fuller. Aniline disulfide is added to lubricating oils to inhibit sludge formation.
- U. S. 2,163,300, June 20, 1939. J. I. Wasson and G. H. B. Davis. Polyhydroxy stearic acid esters are used for stabilizing gasolines colored with dyes.
- U. S. 2,163,640, June 27, 1939. H. Von Bramer and A. C. Ruggles. Condensation products of polyhydric phenols and primary or secondary alkylamines are employed for stabilizing gasolines.
- U. S. 2,165,261, July 11, 1939. A. P. Hewlett and G. E. Phillips. Acetone is added to improve the color stability of kerosene.
- U. S. 2,165,324, July 11, 1939. P. J. Wiezevich and J. I. Wasson. Lubricating oils containing an oxidation inhibitor which also improves the viscosity index.
- U. S. 2,165,651, July 11, 1939. H. V. Rees and J. C. D. Oosterhout. Lecithin and alpha-naphthol are used to improve the stability of gasolines containing tetraethyl lead.
- U. S. 2,167,273, July 25, 1939. E. W. Cook. The oxidation stability of lubricating oils is improved by the addition of alpha-beta-dinaphthylamine.
- U. S. 2,171,780, Sept. 5, 1939. G. W. Ayers, Jr. Dihydroxyphenanthrene is used to retard gum formation in cracked distillates.
- U. S. 2,171,781, Sept. 5, 1939. R. C. Cantelo. Aluminum salt of erucic acid is used to retard sludge formation in lubricating oils.
- U. S. 2,174,248, Sept. 26, 1939. L. A. Mikeska and E. Lieber. Diamyldiphenol disulfide is used to improve the stability of lubricating oils.

- U. S. 2,175,548, Oct. 10, 1939. J. M. Musselman and H. P. Lankelma. Diphenyl carbazide or diphenyl semicarbazide is used to improve the oxidation stability of lubricating oils.
- U. S. 2,175,619, Oct. 10, 1939. G. Rühl. Refining light distillates in the vapor phase with oxygen under the influence of a high-voltage electrostatic field.
- U. S. 2,176,883, Oct. 24, 1939. C. H. Fisher. Tetraalkylhexahydroxy-spirobiindan is used for stabilizing gasolines.
- U. S. 2,178,769, Nov. 7, 1939. P. J. Wizevich. Lubricating oils are extracted with liquid sulfur dioxide or phenol, and the extract material is subjected to a silent electric discharge to obtain materials suitable for improving oxidation stability of lubricating oils.
- U. S. 2,181,121, Nov. 28, 1939. F. B. Downing and C. J. Pedersen. Parabenzyaminophenol is used to improve oxidation stability of cracked distillates sweetened with copper salts.
- U. S. 2,181,122, Nov. 28, 1939. F. B. Downing and C. J. Pedersen. Di-(2-hydroxybenzal)-1,2-diaminobenzene is used to improve the oxidation stability of cracked distillates sweetened with copper salts.
- CHAPTER X.—GUMS IN CRACKED PETROLEUM PRODUCTS.
- U. S. 1,752,945-6, Apr. 1, 1930. W. W. Evans. Ethylene di-para-tolyldiamine is added to oils to improve their stability.
- U. S. 1,776,598, Sept. 23, 1930. J. B. Rather and L. C. Beard, Jr. Preventing discoloration and gum formation of light distillates by blowing them with carbon dioxide to remove dissolved oxygen.
- U. S. 1,789,302, Jan. 20, 1931. W. S. Calcott and I. E. Lee. Preventing gum formation and discoloration of gasoline by adding acetanilide or an aromatic amine.
- U. S. 1,789,413, Jan. 20, 1931. R. C. Osterstrom, J. Hyman, and C. R. Wagner. Removing gum by distilling the oil in the presence of sodium sulfonates.
- U. S. 1,835,184, Dec. 8, 1931. L. Rosenstein and W. J. Hund. The use of a seleno mercaptan, such as phenyl or ethyl, to stabilize gasoline against gum formation.
- U. S. 1,884,559, Oct. 25, 1932. W. S. Calcott and I. E. Lee. Gum formation in gasoline is inhibited by the addition of 0.001-0.1% cresol.
- U. S. 1,884,899, Oct. 25, 1932. E. I. Sollman. Gum formation in gasoline is inhibited by addition of 0.01-0.15% lecithin.
- U. S. 1,904,433, Apr. 18, 1933. H. G. M. Fisher and C. E. Gustafson. Gum formation in gasolines is inhibited by naphthalene, anthracene, or phenanthrene containing hydroxy or amino group in α -position.
- U. S. 1,912,603, June 6, 1933. M. C. Sumpter. Light petroleum distillates are freed from gum- and color-forming constituents by passing their vapors through a mixture of oxychlorides of tin, cadmium or copper, and zinc.
- U. S. 1,914,509, June 20, 1933. A. O. Jaeger. Gum formation in cracked distillates is inhibited by the addition of a phthalide and aniline.
- U. S. 1,916,437, July 4, 1933. J. B. Rather, L. C. Beard, Jr., and O. M. Reiff. Gum formation in light distillates is prevented by the addition of nicotine.
- U. S. 1,916,438, July 4, 1933. J. B. Rather, L. C. Beard, Jr., and O. M. Reiff. Gum formation in light distillates is prevented by the addition of thiocarbanilide.
- U. S. 1,917,648, July 11, 1933. F. E. Kimball. Gum-forming constituents are removed by passing gasoline vapors through a solution of zinc and ammonium chlorides.
- U. S. 1,919,825, July 25, 1933. R. E. Burk. Gum formation is prevented by halogenating a cracked petroleum distillate and then heating it with ammonia.
- U. S. 1,920,248, Aug. 1, 1933. R. B. Day. Gasoline is refined with aqueous hydrochloric acid in the presence of zinc and copper at elevated temperatures and pressures.
- U. S. 1,924,870, Aug. 29, 1933. C. D. Lowry, Jr., and C. G. Dryer. Cracked gasoline is stabilized against gum-for-

- mation by the addition of aldol alpha-naphthyl-amine.
- U. S. 1,935,967, Nov. 21, 1933. C. P. Wilson, Jr. Unstable constituents are removed from cracked distillates by exposing them to elevated temperature and pressure.
- U. S. 1,938,456, Dec. 5, 1933. H. P. Laukelma. Gum formation in cracked distillates is inhibited by the addition of para-acetylaminophenol.
- U. S. 1,939,659, Dec. 19, 1933. W. S. Calcott and H. W. Walker. Gum formation is inhibited by adding to gasolines diarylguanidine salts of acetic, butyric, propionic, stearic, or oleic acid.
- U. S. 1,941,689, Jan. 2, 1934. A. O. Jaeger. Succinimide is added to cracked distillates to inhibit gum formation.
- U. S. 1,945,114, Jan. 30, 1934. A. Lachman. Cracked distillates are refined by passing their vapors through zinc chloride solution.
- U. S. 1,945,521, Feb. 6, 1934. F. B. Downing and H. W. Walker. 4-Hydroxy-1,3-dimethylbenzene or similar xylenols are added to cracked distillates to retard gum formation.
- U. S. 1,947,210, Feb. 13, 1934. P. I. Murrill. Diphenyl-para-phenylenediamine or similar substances are added to cracked distillates to inhibit gum formation.
- U. S. 1,947,869, Feb. 20, 1934. J. C. Morrell and G. Egloff. Cracked distillates are refined by contacting their vapors, mixed with sulfur dioxide and steam, with zinc sulfate.
- U. S. 1,949,896, Mar. 6, 1934. A. P. Bjerregaard. Anthracene or phenanthrene is added to cracked gasoline, and the mixture then contacted with fuller's earth to reduce the gum-forming tendencies.
- U. S. 1,957,134, May 1, 1934. F. B. Downing, R. G. Clarkson, and C. G. Wolff. Gum formation in cracked distillates is inhibited by the addition of compounds such as para-hydroxyanilinoacetonitrile, para-hydroxyanilino dimethylacetonitrile or para-hydroxyanilino hexylacetonitrile.
- U. S. 1,959,315, May 15, 1934. J. B. Rather, L. C. Beard, Jr., and O. M. Reiff. Discoloration and gum formation in cracked distillates is prevented by the addition of a butyl-substituted pyrogallol.
- U. S. 1,959,316, May 15, 1934. J. B. Rather, L. C. Beard, Jr., and O. M. Reiff. Discoloration and gum formation in cracked distillates is prevented by addition of an alkyl-substituted dihydroxybenzene.
- U. S. 1,959,317, May 15, 1934. J. B. Rather, L. C. Beard, Jr., and O. M. Reiff. Discoloration and gum formation in cracked distillates is prevented by the addition of an alkyl-substituted trihydroxybenzene.
- U. S. 1,962,435, June 12, 1934. F. B. Downing and H. W. Walker. Gum formation in gasoline is inhibited by para-hydroxyphenylglycine.
- U. S. 1,966,467, July 17, 1934. D. R. Stevens and W. A. Gruse. Removing gum-forming constituents from cracked distillates by heating their vapors under pressure.
- U. S. 1,966,729, July 17, 1934. J. H. Loomis and J. McKinney. Regeneration of zinc chloride solutions used in refining cracked distillates by extraction with phenolic materials and benzene.
- U. S. 1,969,047, Aug. 7, 1934. K. J. Smith. Cracked gasolines are refined by heating to high temperatures and polymerizing the gum-forming constituents.
- U. S. 1,970,143, Aug. 14, 1934. F. E. Kimball. Gasoline vapors are treated with water solution of calcium and magnesium chlorides and then with a solution of zinc chloride. The treated vapors are then contacted with ammonia and a solution of calcium chloride.
- U. S. 1,970,339, Aug. 14, 1934. T. H. Rogers and V. Voorhees. Gum formation in cracked distillates is prevented by nicotine pyrogallate or amyl gallate.
- U. S. 1,971,329, Aug. 28, 1934. W. S. Calcott and H. W. Walker. Tolylenediamine is used to inhibit gum formation in cracked distillates.
- U. S. 1,975,755, Oct. 2, 1934. L. F. Hoyt and W. A. Smith. Gum formation is inhibited by quinihydrone and anthranilic acid. An aminobenzoic acid or a phenylenediamine may be also used.
- U. S. 1,980,200, Nov. 13, 1934. C. W. Hannum. Gum formation in gasoline

- is inhibited by 4-methyl-benzylamino-phenol.
- U. S. 1,980,201, Nov. 13, 1934. C. W. Hannum. Gum formation in gasoline is inhibited by 4-benzylideneaminophenol.
- U. S. 1,982,267, Nov. 27, 1934. T. H. Rogers and V. Voorhees. A nitroso derivative of a naphthylamine is used to inhibit gum formation in cracked fuels.
- U. S. 1,982,277, Nov. 27, 1934. C. Winning. Gum formation in cracked distillate is inhibited by dinitrosopolyhydroxybenzene, nitrosonaphthol or nitrosoaniline.
- U. S. 1,988,084, Jan. 15, 1935. J. C. Morrell. Cracked distillates are treated in the vapor phase with a solution of zinc chloride in the presence of hydrochloric acid.
- U. S. 1,989,528, Jan. 29, 1935. J. B. Rather, L. C. Beard, Jr., and O. M. Reiff. Ethanolamine is added to cracked gasoline to inhibit gum formation.
- U. S. 1,990,213, Feb. 5, 1935. F. Winkler and H. Häuber. Treatment of gasoline with aluminum chloride for removal of gum-forming constituents.
- U. S. 1,993,941, Mar. 12, 1935. J. C. Morrell and C. G. Dryer. A lignite tar fraction is used to prevent gum formation in gasolines.
- U. S. 1,994,891, Mar. 19, 1935. C. G. Ludeman. Gum formation and discoloration of cracked distillates is prevented by the addition of 4-naphthenyl-pyrogallol.
- U. S. 1,996,075, Apr. 2, 1935. W. K. Lewis and B. Mead. Resorcinol, hydroquinone, or pyrogallol is used to inhibit gum formation in cracked distillates.
- U. S. 1,999,830, W. S. Calcott and I. E. Lee. Gum formation in cracked distillates is inhibited by alkoxy-substituted dihydroxybenzenes, such as pyrogallol-1-methyl ether, methoxy hydroquinone, etc.
- U. S. 2,000,283, May 7, 1935. C. W. Hannum. Gum formation is prevented by adding to cracked distillates 4-cyclohexylaminophenol.
- U. S. 2,002,250, May 21, 1935. C. R. Payne and D. R. Stevens. Cracked distillates are refined with aluminum chloride.
- U. S. 2,002,902, May 28, 1935. S. M. Martin, Jr., and W. A. Gruse. Selective treatment of cracked gasoline fractions to eliminate gum-forming constituents.
- U. S. 2,004,094, June 11, 1935. H. G. M. Fischer and C. E. Gustafson. Phenyl-alpha-naphthylamine is added to cracked distillates to inhibit gum formation.
- U. S. 2,010,029, Aug. 6, 1935. J. C. Morrell and C. G. Dryer. Gum formation in cracked distillates is inhibited by addition of a coal-tar fraction.
- U. S. 2,013,198, Sept. 3, 1935. A. L. Blount. Gum formation in cracked distillates is inhibited by an arsenic or antimony compound, such as para-ethoxyphenylarsine oxide or 2,4-dimethylphenylarsine oxide.
- U. S. 2,014,200, Sept. 10, 1935. F. B. Downing and H. W. Walker. Cracked gasolines are stabilized by the addition of 2,3,4,5- or 2,3,5,6-methyl or ethyl-1-hydroxybenzene.
- U. S. 2,014,923, Sept. 17, 1935. W. L. Benedict. Cracked distillates are stabilized by adding a wood-tar distillate and trianiline.
- U. S. 2,017,756, Oct. 15, 1935. W. J. Bannister. Gum formation in cracked distillates is prevented by addition of a condensation product of ortho-cresol and acetone.
- U. S. 2,019,899, Nov. 5, 1935. H. G. M. Fischer and C. E. Gustafson. Alpha-naphthol or alpha-naphthylamine are used to prevent gum formation in gasolines.
- U. S. 2,023,385, Dec. 3, 1935. L. G. Story. Diaminophenol is added to gasoline to prevent gum formation.
- U. S. 2,023,871, Dec. 10, 1935. L. A. Clarke and C. C. Towne. Monochlorohydroquinone is added to gasoline to retard gum formation.
- U. S. 2,024,681, Dec. 17, 1935. R. F. Davis. Refining cracked distillates with sulfur dioxide and aluminum chloride.
- U. S. 2,025,192, Dec. 24, 1935. F. B. Downing and H. W. Walker. Dihydroxynaphthalene is added to gasoline to inhibit gum formation.
- U. S. 2,027,394, Jan. 14, 1936. E. W. McMullan. Azobenzene, azoxybenzene,

- or hydrazobenzene is added to gasoline to prevent gum formation.
- U. S. 2,027,462, Jan. 14, 1936. E. Ayres and M. L. Hill. Reaction product of di-alpha-naphthylamine and cresol is used as gum inhibitor.
- U. S. 2,028,473, Jan. 21, 1936. P. C. Rich. Revivification of zinc chloride solutions with zinc oxide.
- U. S. 2,029,256, Jan. 28, 1936. R. B. Day. Gasoline is refined at elevated temperatures with hydrochloric acid in the presence of a zinc-bearing clay.
- U. S. 2,029,748, Feb. 4, 1936. H. C. Weber. Prevention of gum formation and discoloration by storing the gasoline in an atmosphere of hydrogen.
- U. S. 2,029,757, Feb. 4, 1936. R. B. Day. Cracked gasoline is treated in the vapor phase with aluminum chloride and zinc.
- U. S. 2,029,758, Feb. 4, 1936. R. B. Day. Refining of cracked distillates with hydrochloric acid in the presence of brass, copper, or zinc.
- U. S. 2,030,033, Feb. 4, 1936. E. B. McConnell. Hydroquinoline or hydroxy-tetrahydroquinone is used as gum inhibitor.
- U. S. 2,030,940, Feb. 18, 1936. T. H. Rogers and V. Voorhees. Aminoazobenzene or hydroxyazobenzene is used to stabilize motor fuels against gum formation.
- U. S. 2,031,917, Feb. 25, 1936. C. Winning, L. E. Sargent, and J. F. Dudley. Monomethylaniline or tricesol is used to retard gum formation in gasolines. A small quantity of a dye capable of acting both as a coloring agent and as an inhibitor is also added.
- U. S. 2,032,787, Mar. 3, 1936. T. W. Bartram. Diaminophenylamine is used to inhibit gum formation in gasoline.
- U. S. 2,033,877, Mar. 10, 1936. R. E. Birk. Amyl mercaptan and di-butylamine are used to retard gum formation in cracked distillates.
- U. S. 2,034,274, Mar. 17, 1936. L. G. Story. Aminoacetophenone is used to prevent discoloration and gum formation in light petroleum distillates.
- U. S. 2,038,614, Apr. 28, 1936. W. A. Gruse. Removal of gum-forming constituents by heating gasoline for 6-30 minutes under pressure at temperatures below cracking.
- U. S. 2,038,630, Apr. 28, 1936. H. T. Bennett and L. G. Story. Catechol is used to inhibit gum formation in gasoline.
- U. S. 2,038,631, Apr. 28, 1936. H. T. Bennett and L. G. Story. Ortho-phenylenediamine is used to inhibit gum formation in gasoline.
- U. S. 2,038,632, Apr. 28, 1936. H. T. Bennett and L. G. Story. Para-phenylenediamine is used to inhibit gum formation in gasoline.
- U. S. 2,039,904, May 5, 1936. J. B. Hill. Removing gum-forming constituents from cracked distillates by contacting their vapors with finely divided adsorbents.
- U. S. 2,044,739, June 16, 1936. D. R. Stevens and C. R. Payne. Removal of gum-forming constituents from gasoline by heating in the presence of polymers obtained from a previous treat.
- U. S. 2,046,907, July 7, 1936. F. Skowronski. Cracked distillates are freed from gum-forming constituents by contacting them with hydrogen chloride and steam in the presence of copper silicate.
- U. S. 2,047,355, July 14, 1936. E. G. Borden. Octyl pyrogallol is used to inhibit gum formation in gasolines.
- U. S. 2,048,770, July 28, 1936. E. Ayres. Alpha-naphthol is added to gasoline to increase the gum-induction period, and phenyl-beta-naphthylamine to lower the rate of gum formation.
- U. S. 2,050,732, Aug. 11, 1936. E. N. Roberts. Cracked gasolines containing inhibitors, such as phenols, amines or aminophenols, are stored over water containing sodium bisulfite, a metal sulfite, or similar substances.
- U. S. 2,052,859, Sept. 1, 1936. C. P. Wilson, Jr. Polyhydric phenols, containing components of turpentine as substituted groups, are added to cracked gasoline to prevent gum formation.
- U. S. 2,053,511, Sept. 8, 1936. H. T. Bennett and L. G. Story. 5-Benzylamino-2-cresol is added to gasoline to prevent gum formation.
- U. S. 2,053,512, Sept. 8, 1936. H. T. Bennett and L. G. Story. 5-amino-2-hydroxytoluene is added to gasoline to prevent gum formation.

- U. S. 2,053,421, Sept. 8, 1936. R. E. Burk and H. P. Lankelma. 1,2-dihydroxyanthraquinone is added to gasoline to prevent gum formation.
- U. S. 2,056,978-9, Oct. 13, 1936. R. C. Osterstrom. Gum-forming constituents are removed by heating and distilling cracked distillates prior to contacting them with fuller's earth.
- U. S. 2,058,881, Oct. 27, 1936. V. Ipatieff. Gum formation in gasoline is inhibited by the addition of reaction products of olefins with wood-tar distillate.
- U. S. 2,060,291, Nov. 10, 1936. G. Egloff. Refining cracked distillates by heating with zinc chloride solutions.
- U. S. 2,062,201, Nov. 24, 1936. T. W. Bartram. Phenoxazine is used to inhibit gum formation in cracked distillates.
- U. S. 2,063,516, Dec. 8, 1936. J. C. Morrell. Phthalic acid, phthalic anhydride, or a phthalide is used to prevent gum formation in cracked distillates and retard the deterioration of their anti-detonating properties in storage.
- U. S. 2,063,518, Dec. 8, 1936. J. C. Morrell and G. Egloff. Cracked distillates are treated at elevated temperatures with hydrochloric acid and zinc chloride.
- U. S. 2,063,522, Dec. 8, 1936. R. C. Osterstrom. Cracked distillates are improved in color and gum stability by contacting their vapors with liquid polymers.
- U. S. 2,065,249, Dec. 22, 1936. J. P. Smoots. Alpha-naphthol and an amine are used as gum inhibitors in motor fuels.
- U. S. 2,065,568, Dec. 29, 1936. H. W. Elley and H. W. Walker. Gum formation in motor fuels is inhibited by the addition of 1-amino-2-naphthol.
- U. S. 2,068,850, Jan. 26, 1937. C. Ellis. Gum formation in cracked distillates is retarded by treating them at elevated temperatures with maleic anhydride, fumaric acid, quinone, acrolein, or similar substances, followed by washing with sodium hydroxide solutions.
- U. S. 2,070,304, Feb. 9, 1937. A. O. Jaeger. Gum formation is inhibited by adding to gasoline benzamide or phthalamide.
- U. S. 2,070,978, Feb. 16, 1937. J. P. Smoots. Inhibiting gum formation in cracked distillates by the addition of a di-hydroxy aromatic compound, such as catechol, and an aromatic amine.
- U. S. 2,071,064, Feb. 16, 1937. F. B. Downing and R. G. Clarkson. Gum formation in cracked distillates is inhibited by addition of para-hydroxy-N-phenylmorpholine.
- U. S. 2,074,467, Mar. 23, 1937. C. L. Gutzeit. Amylated para-amino-phenol is used to inhibit gum formation in cracked distillates.
- U. S. 2,076,524, April 13, 1937. F. B. Behrens. Deteriorated cracked gasoline containing organic peroxides formed during the deterioration, is restored by treating with burned magnesite.
- U. S. 2,080,681, May 18, 1937. J. R. Wilson and V. Voorhees. Alkylated naphthalene is used to prevent gum formation in gasoline.
- U. S. 2,080,928, May 18, 1937. T. H. Rogers and V. Voorhees. Methyl- or ethyl-phenylenediamine is added to inhibit gum formation in gasoline.
- U. S. 2,081,130, May 25, 1937. H. V. Atwell. Gum formation in combustible gases is retarded by para-benzylaminophenol.
- U. S. 2,081,218, May 25, 1937. R. E. Burk. Cracked distillates are stabilized by heat treatment.
- U. S. 2,083,197, June 8, 1937. C. D. Lowry, Jr., and C. G. Dryer. Gum formation is retarded by adding to cracked distillates a reaction product of tar with alkyl halides.
- U. S. 2,084,754, June 22, 1937. C. P. Wilson, Jr. Gum formation is inhibited by adding to gasoline a reaction product of pyrogallol and a liquid sulfur dioxide extract from naphtha.
- U. S. 2,084,977, June 22, 1937. T. H. Rogers and V. Voorhees. A butyl substituted aminophenol is used to inhibit gum formation in cracked distillates.
- U. S. 2,087,597, July 20, 1937. C. L. Gutzeit. Oxazine is added to gasoline to inhibit gum formation.
- U. S. 2,094,554, Sept. 28, 1937. L. G. Story. Aromatic coal- or wood-tar is used to inhibit gum formation in cracked distillates.

- U. S. 2,094,585, Oct. 5, 1937. W. A. Craig. Refining cracked distillates in the vapor phase with zinc chloride solution containing calcium chloride.
- U. S. 2,094,586, Oct. 5, 1937. W. A. Craig. Refining cracked distillates in the vapor phase with zinc chloride solution containing a petroleum base hydrochloride.
- U. S. 2,095,211, Oct. 5, 1937. L. P. Chebotar. Gum formation is inhibited by adding an indophenol dye to a cracked distillate.
- U. S. 2,096,163, Oct. 19, 1937. R. B. Day. Refining cracked distillates in the liquid phase at elevated temperatures and under pressure with zinc chloride in the presence of hydrogen chloride and steam.
- U. S. 2,096,798, Oct. 26, 1937. W. F. Faragher. Refining cracked distillates with aluminum or zinc chloride in the vapor phase.
- U. S. 2,097,773, Nov. 2, 1937. J. W. Orclup. Gasoline is colored with an acridine dye and stabilized with aluminum stearate.
- U. S. 2,107,147, Feb. 1, 1938. H. W. Elley and H. W. Walker. Gum formation in cracked distillates is inhibited by adding a hydroxydiphenylamine.
- U. S. 2,122,408, July 5, 1938. H. T. Clarke and F. R. Bean. Di-butyl ester of para-hydroxyphenyliminodiacetic acid is used to retard gum formation in cracked distillates.
- U. S. 2,134,434, Oct. 25, 1938. T. L. Cantrell and J. O. Turner. Alkylphenoxy derivatives of *m*-dinitrobenzene are used as oxidation or gum inhibitors.
- U. S. 2,134,959, Nov. 1, 1938. R. L. Sibley. Cracked distillates are stabilized against gum formation by the addition of diphenyl guanidine acid phthalate, aniline acid phthalate, and similar substances.
- U. S. 2,137,175, Nov. 15, 1938. G. D. Martin. Gum formation in cracked distillates is inhibited with cyclohexyldine-para-aminophenol.
- U. S. 2,148,758, Feb. 28, 1939. H. P. Iankelma. Benzyl-1,2-dihydroxybenzene is used to stabilize cracked distillates against gum formation.
- U. S. 2,149,351, Mar. 7, 1939. E. H. Lang and R. C. Osterstrom. Cracked distillates are stabilized by heat treatment, followed by redistillation.
- U. S. 2,149,759, Mar. 7, 1939. T. L. Cantrell. Gum formation in cracked distillates is inhibited by the addition of reaction products formed from phenol and olefins by the action of sulfuric acid.
- U. S. 2,180,324, Nov. 14, 1939. R. C. Osterstrom. Cracked distillates are refined by heating to elevated temperatures and under pressure.

CHAPTER XI.—DETERIORATION OF LUBRICATING AND SIMILAR OILS.
ADDITION AGENTS.

- U. S. 22,621, Jan. 18, 1859. R. R. Brown. Preparing lubricants containing elemental sulfur.
- U. S. 29,243, July 24, 1860. C. Chitterling. Lubricant containing sulfur, oxalic acid, etc.
- U. S. 41,068, Jan. 5, 1864. W. Hilton. Lubricant containing elemental sulfur.
- U. S. 60,829, Jan. 1, 1867. J. F. Boynton. Lubricant containing elemental sulfur.
- U. S. 76,838, Apr. 14, 1868. G. O. Spence. Lubricant containing elemental sulfur.
- U. S. 97,262, Nov. 23, 1869. C. S. Moore. Lubricant containing elemental sulfur.
- U. S. 112,453, Mar. 7, 1871. E. Q. Henderson. Lubricant containing elemental sulfur.
- U. S. 120,631, Nov. 7, 1871. G. M. Denison. Lubricant containing elemental sulfur.
- U. S. 132,379, Oct. 22, 1872. J. Williams. Lubricant containing elemental sulfur.
- U. S. 134,890, Jan. 14, 1873. H. R. Hutchinson. Lubricant containing elemental sulfur.
- U. S. 156,714, Nov. 10, 1874. J. Scott. Lubricant containing elemental sulfur.
- U. S. 157,848, Dec. 15, 1874. A. G. Mandel. Lubricant containing elemental sulfur.
- U. S. 164,117, June 8, 1875. J. Williams. Lubricant containing elemental sulfur.
- U. S. 167,730, Sept. 14, 1875. B. F. Bartlett. Lubricant containing elemental sulfur.

- U. S. 170,581, Nov. 30, 1875. J. F. Mendonsa. Lubricant containing elemental sulfur.
- U. S. 179,744, July 11, 1876. J. G. Upper. Lubricant containing elemental sulfur.
- U. S. 199,789, Jan. 29, 1878. R. J. Chard. Lubricant containing elemental sulfur.
- U. S. 250,009, Nov. 22, 1881. E. Smalley. Lubricant containing elemental sulfur.
- U. S. 287,643, Oct. 30, 1883. G. Dimick. Lubricant containing elemental sulfur.
- U. S. 919,506, Apr. 27, 1909. W. R. Whitney. Lowering pour point of heavy oils by addition of benzyl chloride.
- U. S. 1,018,971, Feb. 27, 1912. T. S. Hamilton. Oils are refined by emulsifying with sodium chloride solution and settling.
- U. S. 1,234,862, July 31, 1917. A. L. Brown. Treating oil with 0.1-0.2% of red phosphorus to prevent sludging on exposure to air.
- U. S. 1,286,091, Nov. 6, 1918. A. Philip. Reducing the viscosity of a heavy fuel oil by blending it with 8% or less of naphthalene.
- U. S. 1,319,129, Oct. 21, 1919. J. E. Southeombe and H. M. Wells. Adding oleic or similar acids to lubricating oils to decrease the friction coefficient.
- U. S. 1,472,882, Nov. 6, 1923. H. R. Moody. Producing non-sludging oils by hydrogenation with nascent hydrogen, obtained by treating an alkali hydroxide with a suitable metal.
- U. S. 1,601,753, Oct. 5, 1926. T. Hellthaler. Decolorizing dark lubricating oils with about 5% of antimony pentachloride.
- U. S. 1,643,272, Sept. 20, 1927. T. Hellthaler. Treating oils with titanium chloride distributed over fuller's earth or other substance.
- U. S. 1,742,020, Dec. 31, 1929. A. H. Ackerman. Reducing the viscosity of cracked residuum by treating with a mixture of anthracene, nitrobenzene, sodium hydroxide, and naphthalene.
- U. S. 1,752,309, Apr. 1, 1930. R. R. Rosenbaum. A metal ricinoleate is added to lubricating oils to improve their stability.
- U. S. 1,762,902, June 10, 1930. J. F. Werder. Lubricating oils are saturated with carbon dioxide before they are charged to engines.
- U. S. 1,774,845, Sept. 2, 1930. T. H. Rogers. Turbine oils are stabilized with diphenylamine, gallic acid or dibutylresorcinol.
- U. S. 1,787,951, Jan. 6, 1931. W. Pungs and E. Frese. Improving the viscosity and lubricating properties of oils by adding montan wax bleached with chromic acid.
- U. S. 1,793,134, Feb. 17, 1931. T. H. Rogers. Prevention of acid-formation and emulsification of turbine oils by adding small quantities of naphthol.
- U. S. 1,793,135, Feb. 17, 1931. T. H. Rogers. Prevention of acid-formation and emulsification of turbine oils by adding about 0.04% of pyrogallol or similar polyhydroxy aromatic compounds.
- U. S. 1,811,243, June 23, 1931. J. H. Osmer. Refining lubricating oils with aluminum chloride.
- U. S. 1,826,439, Oct. 6, 1931. D. Stryker. Improving lubrication of pistons by adding 0.2-1% of oxidized paraffin wax to gasoline.
- U. S. 1,839,012, Dec. 29, 1931. J. C. Black, W. D. Rial, and J. R. McConnell. Refining and imparting green fluorescence to lubricating oils by treating them with adsorbents in the presence of a coal-tar distillate which contains the fluorescent bodies. Treating is preferably done at 390-600° F.
- U. S. 1,841,070, Jan. 12, 1932. B. W. Story. Addition of cetyl alcohol to transformer oils to inhibit sludge formation.
- U. S. 1,841,754, Jan. 19, 1932. J. M. Michel. Removing phosphorus from used oils by treating with a metal capable of reacting with phosphorus, such as copper, at elevated temperatures.
- U. S. 1,842,856, Jan. 26, 1932. J. C. Black, W. D. Rial, and J. R. McConnell. Imparting green fluorescence to lubricating oils by adding an extract from a coal-tar residuum.
- U. S. 1,857,404, May 10, 1932. J. E. Schott. Dewaxing by adding to the lubricating oil a petroleum distillation residue of high specific gravity to cause wax agglomeration, and wax is then removed.

- U. S. 1,909,295, May 16, 1933. M. Luther and H. Wille. Sulfonated products similar to Turkey-red oil are produced by oxidizing wax with air and treating the oxidized materials with sulfuric acid.
- U. S. 1,919,669, July 25, 1933. C. J. Rodman and R. P. Dummire. Transformer oils are freed from air and moisture by spraying them into vacuum.
- U. S. 1,932,381, Oct. 24, 1933. B. Galls-worthy. Lubricating oils are improved by adding to them 1 to 5% of oxidized paraffin wax treated with fuller's earth.
- U. S. 1,934,043, Nov. 7, 1933. G. H. B. Davis. The viscosity index of a lubricating oil is improved by treating it with an activated material prepared by mixing petrolatum with aluminum chloride and separating the sludge.
- U. S. 1,945,614, Feb. 6, 1934. B. H. Lincoln. A deflocculating agent is added to lubricating oil. The agent is prepared by treating oleic acid with nitric acid.
- U. S. 1,948,163-4, Feb. 20, 1934. U. B. Bray and C. E. Swift. Preparation of lubricating oils by refining with aluminum chloride.
- U. S. 1,963,489, June 19, 1934. E. W. Fuller and B. W. Story. Petroleum wax is stabilized by addition of isomanyl-disulfide, butyl disulfide, or methyl-phenyl disulfide.
- U. S. 1,972,760, Sept. 4, 1934. W. S. Calcott and I. E. Lee. Diphenylguanidine or di-ortho-tolylguanidine is used as gum inhibitor in cracked distillates.
- U. S. 1,998,350, Apr. 16, 1935. C. Wulff, F. Moll and W. Breuers. Viscosity index of lubricating oils is improved by the addition of 0.5-2% of polymerized styrene.
- U. S. 2,010,387, Aug. 6, 1935. E. Ayres and H. G. Smith. Improving lubricating oils by treatment with aluminum chloride in the presence of a low boiling point halogenated hydrocarbon.
- U. S. 2,012,918, Aug. 27, 1935. B. H. Shoemaker. Dibutyl sodamide, diethyl sodamide or ethyl propyl sodamide is added to lubricating oil to prevent sludging.
- U. S. 2,025,387, Dec. 24, 1935. J. M. Harris, Jr. Improving lubricating properties of oils by oxidizing them with air at elevated temperatures.
- U. S. 2,031,986, Feb. 25, 1936. R. K. Stratford and J. L. Huggett. Stable lubricating oils are produced by addition of a lead or aluminum soap and phenol, cresol, xylene, or alpha-naphthol.
- U. S. 2,043,923, June 9, 1936. A. W. Burwell. Improving lubricating qualities of oils by the addition of oxidation products of scale wax, amorphous wax, and liquid hydrocarbons.
- U. S. 2,050,139, Aug. 4, 1936. E. Wana-maker and H. D. Allgeo. Film strength of lubricating oils is improved by heating the oils with aluminum hydroxide at 158-205° F.
- U. S. 2,057,212, Oct. 13, 1936. B. H. Shoemaker and K. Taylor. Lubricating oils are made resistant to sludge formation through the addition of alkali metal alcoholates, such as sodium propylate, potassium amylate, etc.
- U. S. 2,070,567, Feb. 16, 1937. C. E. Adams. Improving the viscosity index of lubricating oils by the partial oxidation with oxygen in the presence of ferric chloride, followed by refining with liquid propane.
- U. S. 2,070,627, Feb. 16, 1937. B. H. Shoemaker. Improving viscosity index of lubricating oils by partial oxidation of the oils with oxygen at elevated temperatures.
- U. S. 2,081,075, May 18, 1937. A. C. Vobach. Calcium phenyl stearate is used in lubricating oils to decrease sludge formation in service.
- U. S. 2,083,139, June 8, 1937. W. G. Black. Lubricating properties are improved by adding to the oils a product obtained by heating the oil with naphthalene, nitrobenzene, rubber, and dimethylaniline.
- U. S. 2,084,270, June 15, 1937. B. H. Shoemaker. Di- and tri-butyl or amyl phosphite is added to lubricating oil to inhibit corrosion.
- U. S. 2,085,759, July 6, 1937. L. Laskaris. The fluorescence of lubricating oils is improved by adding a coal-tar pitch which has been heated in the presence of sodium hydroxide.
- U. S. 2,086,399, July 6, 1937. C. C. Towne. The viscosity index of lubricating oils is improved by addition of

- a reaction product of rubber with metal halides and halogen acids.
- U. S. 2,087,603, July 20, 1937. L. A. Mikeska and C. F. Smith. Hydrogenated menhaden oil slightly oxidized with oxygen is added to mineral oils to improve their oiliness.
- U. S. 2,088,193, July 27, 1937. W. L. Evers. Oiliness is improved by adding to lubricating oil a reaction product of stannic chloride with a mercaptan-substituted fatty acid.
- U. S. 2,094,097, Sept. 28, 1937. F. B. Downing and A. F. Benning. Oiliness is improved by adding to lubricating oils 2,4-dinitrophenyl thiocyanate.
- U. S. 2,094,593, Oct. 5, 1937. E. W. Gardiner, J. W. Greene and A. L. Lyman. Lubricating oils of high viscosity index are obtained by chlorinating and then dechlorinating the straight chain hydrocarbons.
- U. S. 2,095,538, Oct. 12, 1937. A. C. Vobach. Calcium phenyl stearate is added to diesel engine lubricating oils.
- U. S. 2,096,390, Oct. 19, 1937. A. W. Burwell and A. Kempe. Improving lubricating characteristics of oils by adding esters produced by condensing methyl, ethyl, or propyl alcohols with oxidation products of hydrocarbon oils.
- U. S. 2,097,245, Oct. 26, 1937. C. C. Towne. Imparting fluorescence to lubricating oils with the heavy condensate arising from cracking hydrocarbon gases.
- U. S. 2,096,905, Oct. 26, 1937. E. Lieber. Oiliness and resistance to oxidation are improved by adding to lubricating oils esters containing sulfur, selenium, or tellurium which is directly connected to an aromatic ring.
- U. S. 2,104,097, Jan. 4, 1938. M. Pier, W. Hirschberger and H. Lemme. Improving bloom of lubricating oils by adding a residue from vacuum distillation of a deasphalted product obtained from destructive hydrogenation of coal.
- U. S. 2,106,232, Jan. 25, 1938. H. Zorn and W. Rosinsky. A polymer of isobutylene is added to a lubricating oil in the presence of aluminum chloride in order to improve the viscosity index of the oil.
- U. S. 2,106,554, Jan. 25, 1938. B. H. Lincoln and A. Henriksen. Oiliness is improved by adding a chlorinated oxidized hydrocarbon oil to a lubricant.
- U. S. 2,106,767, Feb. 1, 1938. L. B. Smith, S. R. Funsten, and H. W. Field. Fluorescence of oils is increased by adding a coal-tar residue which has been heated in contact with unsaturated hydrocarbons.
- U. S. 2,107,905, Feb. 8, 1938. A. W. Ralston and C. W. Christensen. Film strength of lubricating oils is improved by the addition of mono- and di-chlorinated derivatives of xylyl heptadecyl ketone and similar substances.
- U. S. 2,109,357, Feb. 22, 1938. B. H. Lincoln and A. Henriksen. Chlorinated carnauba wax is added to lubricating oils to improve their film strength.
- U. S. 2,109,463, Mar. 1, 1938. T. L. Cantrell and J. O. Turner. Ethyl-, propyl-, butyl- or amyl-thioether of anthraquinone is added to lubricating oils to prevent corrosive action on cadmium bearings.
- U. S. 2,109,645, Mar. 1, 1938. H. P. Lanckelma. Small quantities of furfural are added to naphtha, and small quantities of phenol are added to lubricating oils for identification purposes.
- U. S. 2,109,772, Mar. 1, 1938. P. K. Frolich. Viscosity index of lubricating oils is improved by addition of condensation products of olefins and diolefins present in cracked naphtha.
- U. S. 2,111,126, Mar. 15, 1938. H. Rabe. Fluorescence of mineral oils is improved by adding a hydrogenated condensation product of a cracked distillate and naphthalene.
- U. S. 2,111,990, Mar. 22, 1938. J. A. Reid and G. H. Short. Mercapto benzothiazole is added to corrosive gasoline to reduce its corrosiveness.
- U. S. 2,112,109, Mar. 22, 1938. W. J. Marsh. Chloronaphthalene composition is added to lubricating oils to improve their film strength.
- U. S. 2,112,305, Mar. 29, 1938. R. Rosen. Lubricating oils are improved by the addition of tetracresyl bismuth, trimethyltriphenylstannate or tetramethyl mercury.
- U. S. 2,113,752, Apr. 12, 1938. P. J. Wiezevich. Acetic esters of mono-

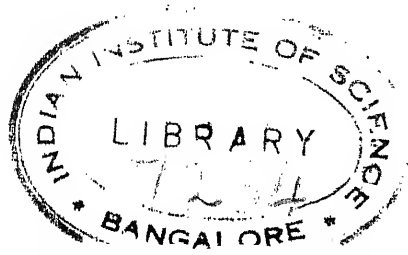
- hydric alcohols are used to improve lubricating properties of oils.
- U. S. 2,113,754, Apr. 12, 1938. J. C. Zimmer and A. J. Morway. Butyl furate is used to improve lubricating properties of oils.
- U. S. 2,114,525, Apr. 19, 1938. E. Eichwald. Polymerized fatty oils are used to improve viscosity index of lubricating oils.
- U. S. 2,115,341, Apr. 26, 1938. L. A. Mikeska and L. B. Turner. Acetylated castor oil is used to improve oiliness of lubricating oils.
- U. S. 2,115,354, Apr. 26, 1938. J. I. Wasson. Soybean oil and isopropyl alcohol are used to improve lubricating oils.
- U. S. 2,117,076, May 10, 1938. H. T. Bennett and C. Prather. Lubricating oils are improved in film strength by addition of alpha-hydroxybiphenyl.
- U. S. 2,118,214-7, May 24, 1938. W. J. Marsh and J. A. Spina. Improving film strength of lubricating oils by addition of chlorinated benzene.
- U. S. 2,119,097, May 31, 1938. E. W. Carlson. Fluorescence is imparted to lubricating oils by the addition of a heavy condensate obtained by heating gaseous hydrocarbons to elevated temperature under pressure.
- U. S. 2,119,149, May 31, 1938. W. T. Bishop. Stabilization of chlorinated paraffin wax with sodium hydroxide solution, followed by extraction with toluene. The product is used for improving film strength of lubricating oils.
- U. S. 2,119,403, May 31, 1938. O. E. Roberts, Jr. Lubricating oils are stabilized by refining with ammonium nitrate, followed by treating the distillate with ammonium chloride at above 435 °F.
- U. S. 2,119,556, June 7, 1938. C. F. Prutton. Stabilized halogenated paraffin wax is used to improve film strength of lubricating oils.
- U. S. 2,121,976, June 28, 1938. L. A. Mikeska and C. A. Cohen. A wool oil acetic ester is used to improve oiliness of lubricating oils.
- U. S. 2,123,641, July 12, 1938. P. J. Wiezevich. A polymer obtained by the interreaction of a polyhydroxy alcohol and 12-hydroxystearic acid is used to improve the viscosity index of lubricating oils.
- U. S. 2,124,598, July 26, 1938. L. B. Turner. Film strength of lubricating oils is improved by the addition of chlorinated paraffin wax treated with an inorganic polysulfide.
- U. S. 2,125,169, July 26, 1938. W. J. Marsh. A partially hydrogenated and chlorinated petroleum product is used to improve film strength of lubricants.
- U. S. 2,125,305, Aug. 2, 1938. T. G. Murphy. Alkali metal mahogany sulfonates are added to lubricating oils to prevent corrosion.
- U. S. 2,125,851, Aug. 2, 1938. A. W. Ralston. Polymerized stearonitrile is added to improve lubricating properties of oils.
- U. S. 2,125,934, Aug. 9, 1938. L. Libberthson. A copper mahogany sulfonate is added to lubricating oils to prevent corrosion.
- U. S. 2,125,935, Aug. 9, 1938. L. Libberthson. A cadmium mahogany sulfonate is added to lubricating oils to prevent corrosion.
- U. S. 2,126,590, Aug. 9, 1938. J. Valentin. Halogenated petroleum wax is employed to improve film strength of lubricating oils.
- U. S. 2,128,574, Aug. 30, 1938. A. J. van Peski and W. Coltof. Acids obtained by the oxidation of a synthetic hydrocarbon oil obtained by polymerizing olefins are used to improve the lubricating and anticorrosive properties of lubricating oils.
- U. S. 2,129,281, Sept. 6, 1938. B. H. Lincoln and G. D. Byrkit. Film strength of lubricating oils is improved by the addition of para-tolyl silicon trichloride.
- U. S. 2,131,138, Sept. 27, 1938. A. E. Ganzert. Aluminum stearate, zinc oxide, and zinc stearate are added to improve the friction coefficient of lubricating oils.
- U. S. 2,132,847, Oct. 11, 1938, M. A. Dietrich. Unvulcanized rubber which has been plasticized with thio-beta-naphthol is added to lubricating oils to improve their viscosity index.
- U. S. 2,133,493, Oct. 18, 1938. J. I. Wasson. Lubricating oils containing a

- polymerization product of rapeseed or fish oil and a small quantity of sulfur, selenium, or tellurium as addition agent.
- U. S. 2,133,734, Oct. 18, 1938. F. R. Moser. Lubricants are rendered non-corrosive by an alkyl or alkylene succinic acid.
- U. S. 2,134,436, Oct. 25, 1938. T. L. Cantrell and J. O. Turner. An alkyl phenyl ether of 2,4-dinitrophenol is used to improve the film strength of lubricants.
- U. S. 2,134,554, Oct. 25, 1938. L. P. Grobel. Film strength of lubricating oils is improved by benzaldehyde, salicyl aldehyde, or benzoic acid.
- U. S. 2,135,092, Nov. 1, 1938. G. M. Maverick. Improving a lubricating oil by adding a thickening polymer of the linear hydrocarbon type, an oxidation inhibitor, such as naphthyl disulfide, and a sludge disperser, such as a petrolatum condensation product resulting from high frequency discharges.
- U. S. 2,137,727, Nov. 22, 1938. E. F. Quirke. Fuel oils are stabilized with naphthalene, sodium phosphate and sodium hydroxide.
- U. S. 2,137,777, Nov. 22, 1938. B. H. Lincoln, W. L. Steiner and A. Henriksen. Oiliness of lubricating oils is increased by the addition of a chlorinated alcohol.
- U. S. 2,137,782, Nov. 22, 1938. C. F. Prutton and A. K. Smith. Oiliness of lubricating oils is improved by the addition of a chlorinated and oxygen-containing hydrocarbon.
- U. S. 2,137,783, Nov. 22, 1938. C. F. Prutton and A. K. Smith. Oiliness of lubricating oils is improved by the addition of a chlorinated diphenyl ether.
- U. S. 2,137,784, Nov. 22, 1938. C. F. Prutton and A. K. Smith. Oiliness of lubricating oils is improved by the addition of a halogenated dicyclohexyl ether.
- U. S. 2,138,835, Dec. 6, 1938. J. G. Butz. Phosphine oxide or sulfide is added to lubricating oil to improve the film strength.
- U. S. 2,139,086, Dec. 6, 1938. A. W. Lewis. Ethylene cyanide is added to lubricating oils to reduce their corrosiveness.
- U. S. 2,139,087, Dec. 6, 1938. A. W. Lewis. Cyanoacetamide is used to reduce the corrosiveness of lubricating oils.
- U. S. 2,139,088, Dec. 6, 1938. A. W. Lewis. Aminoacetonitrile is used to reduce the corrosiveness of lubricating oils.
- U. S. 2,139,335, Dec. 6, 1938. B. H. Shoemaker. Butyl alpha-isothiocyanamyl ether is added to lubricating oils to prevent corrosion.
- U. S. 2,139,668, Dec. 13, 1938. F. W. Breth and A. Kinsel. Oiliness is improved by adding to a lubricating oil the residue obtained after exhaustive extraction of Pennsylvania residuum with acetone.
- U. S. 2,139,725, Dec. 13, 1938. E. W. Cook. Triphenylarsine sulfide is used to reduce the corrosiveness of lubricating oils.
- U. S. 2,139,726, Dec. 13, 1938. E. W. Cook. Para-ethoxyphenylmorpholine is used to reduce corrosiveness of lubricating oils.
- U. S. 2,139,758, Dec. 13, 1938. A. W. Lewis. Benzanilide is used to reduce the corrosiveness of lubricating oils.
- U. S. 2,141,142, Dec. 20, 1938. A. W. Ralston. Film strength of lubricating oils is improved by adding a reaction product of sulfur chloride and an aliphatic nitrile.
- U. S. 2,142,327, Jan. 3, 1939. J. M. Muselman. Viscosity of lubricating oils is increased by addition of rubber.
- U. S. 2,142,916, Jan. 3, 1939. G. L. Parkhurst. Film strength of lubricating oils is improved by heating them with sulfur and then extracting with Chlorex.
- U. S. 2,143,142, Jan. 10, 1939. M. A. Dietrich. A hydroxylated acetal is used to improve the film strength and stability of lubricating oils.
- U. S. 2,144,078, Jan. 17, 1939. G. L. Neely. Lubricating oils are improved with respect to ring sticking by the addition of aluminum naphthenate.
- U. S. 2,144,469, Jan. 17, 1939. W. E. Townsend and R. O. Maxwell. Rapeseed oil, castor oil, and zinc or aluminum stearate are added to lubricating oils to improve their characteristics.
- U. S. 2,144,652, Jan. 24, 1939. L. D. Fulton and J. M. Hinman. Improving

- the viscosity index of lubricating oils by incorporating into them the high viscosity index constituents occluded by the petrolatum.
- U. S. 2,144,773, Jan. 24, 1939. R. W. Provine and H. T. Bennett. Corn oil is used to improve the viscosity index and stability of lubricating oils.
- U. S. 2,144,855, Jan. 24, 1939. J. T. Rutherford and H. A. Francis. Lubricating oils containing aluminum naphthenate are heated to above 212° F. in contact with steam to break the viscosity.
- U. S. 2,146,543, Feb. 7, 1939. W. H. James, R. C. Moran, and W. L. Evers. A reaction product of phosphorus trichloride and aniline is used to reduce corrosiveness of lubricating oils.
- U. S. 2,146,584, Feb. 7, 1939. D. Lipkin. A reaction product of an aliphatic amine with phosphorus trichloride, phosphorus oxychloride, phosphorus tri- or penta sulfide, or phosphorus chlorosulfide is used to improve the film strength of lubricating oils.
- U. S. 2,147,155, Feb. 14, 1939. R. H. Gardner. Calcium phenyl stearate and elemental sulfur are added to lubricating oils as addition agents.
- U. S. 2,147,578, Feb. 14, 1939. W. B. Hendrey. Film strength of lubricating oils is improved by adding a reaction product of naphthalene and sulfur.
- U. S. 2,147,647, Feb. 21, 1939. A. H. Gleason. An autocondensation product of 12-hydroxystearic acid is added to lubricating oils to improve their viscosity index.
- U. S. 2,147,713, Feb. 21, 1939. J. W. Orelup. Fluorescent material for lubricating oils is prepared by heating a water-insoluble soap of a high fatty acid with acridine, rhodamine, eosine, or eurhodine dyes.
- U. S. 2,149,271, Mar. 7, 1939. J. G. Butz. Triphenylphosphine is added to lubricating oils to improve their film strength.
- U. S. 2,149,788, Mar. 7, 1939. A. S. Orr. Benzene or toluene sulfonyl chloride is used to reduce corrosiveness of lubricating oils.
- U. S. 2,149,856, Mar. 7, 1939. L. J. McKone and W. E. Lyons. Formation of hard carbon deposits in engines is prevented by adding to lubricating oils a beta-diketone of platinum, palladium, cobalt, nickel, uranium, zinc, molybdenum, copper, iron, or tungsten and a beta-diketone of cerium, thorium, zirconium, beryllium, barium, chromium, titanium, vanadium, cesium, boron, aluminum, or lanthanum.
- U. S. 2,149,857, Mar. 7, 1939. L. A. Mikeska and R. Rosen. Oiliness is improved by adding to lubricating oils a condensation product of diolefins with maleic anhydride.
- U. S. 2,150,177, Mar. 14, 1939. B. H. Lincoln and G. D. Byrkit. Film strength of lubricating oils is improved by adding a phenylated and chlorinated aliphatic derivative.
- U. S. 2,150,363, Mar. 14, 1939. O. H. Dawson. Fluorescent material is prepared by cracking petroleum solvent extracts.
- U. S. 2,151,300, Mar. 21, 1939. R. C. Moran and A. P. Kozacik. An alkyl phosphite and cyclohexylamine are used to improve lubricating oil characteristics.
- U. S. 2,152,683, Apr. 4, 1939. E. Eichwald. Polymerization product of oleic acid and glycerol or sorbitol is used to improve the viscosity index of lubricating oils.
- U. S. 2,153,482, Apr. 4, 1939. C. F. Prutton. Dibenzyl sulfide containing chlorine is used to improve film strength of lubricants.
- U. S. 2,154,096, Apr. 11, 1939. C. M. Loane. Tributyl- or triphenyl-thiazole or similar compounds are added to lubricating oils to reduce their corrosiveness.
- U. S. 2,154,097, Apr. 11, 1939. C. M. Loane. A mercaptobenzothiazole is added to lubricating oils to reduce their corrosiveness.
- U. S. 2,154,098, Apr. 11, 1939. C. M. Loane and B. H. Shoemaker. Chloropropyl borate is used to improve the film strength of lubricating oils.
- U. S. 2,156,803, May 2, 1939. H. S. Cooper and V. R. Damerell. Molybdenum sulfide is used to improve the film strength of lubricating oils.
- U. S. 2,157,078, May 2, 1939. B. H. Lincoln and G. D. Byrkit. Dichlorohydroquinone distearate is used to im-

- prove the film strength of lubricating oils.
- U. S. 2,157,079, May 2, 1939. B. H. Lincoln and G. D. Byrkit. Trichlorophenyl stearate is used to improve the film strength of lubricating oils.
- U. S. 2,157,452, May 9, 1939. R. L. Humphreys. Triphenyl or triamyl thiophosphate is used to improve the film strength of lubricating oils.
- U. S. 2,157,479, May 9, 1939. T. L. Cantrell and J. G. Peters. Butene is reacted with phenol in the presence of sulfuric acid and then with phosphorus trichloride and ammonia in order to obtain a stabilizing agent and corrosion inhibitor for lubricating oils.
- U. S. 2,157,873, May 9, 1939. A. J. van Peski and F. R. Moser. Cupro-bromide or butyl sulfide and alkenyl succinic acid are used to improve film strength of lubricating oils as in extreme pressure lubricants.
- U. S. 2,158,096, May 16, 1939. J. H. Wernitz. Octyl acid phthalate, naphthenyl acid phthalate, and similar substances are used to improve the film strength of lubricating oils.
- U. S. 2,158,389, May 16, 1939. C. C. Towne. Acetone or butyl alcohol extract of blown rapeseed oil or polymerized perilla oil is used to improve the viscosity index of lubricating oils.
- U. S. 2,160,293, May 30, 1939. B. H. Shoemaker and C. M. Loane. Heterocyclic compounds are used to prevent corrosiveness of lubricating oils.
- U. S. 2,160,880, June 6, 1939. C. M. Loane and B. H. Shoemaker. Tin diamyldithiocarbamate is used to render lubricating oils noncorrosive.
- U. S. 2,160,881, June 6, 1939. C. M. Loane and B. H. Shoemaker. Organic esters of selenic acid are used to render lubricating oils noncorrosive.
- U. S. 2,160,915, June 6, 1939. W. Schreiber. Phenyl 1,4-phosphoxane is used to improve the film strength of lubricating oils.
- U. S. 2,160,917, June 6, 1939. B. H. Shoemaker and C. M. Loane. Tributyl borate, tributyl thioborate, triphenyl borate, and similar compounds are added to lubricating oils to minimize corrosion.
- U. S. 2,161,184, June 6, 1939. L. J. McKone and W. E. Lyons. A beta-diketone of platinum, palladium, or nickel is added to lubricating oils to prevent formation of hard carbon deposits in engines.
- U. S. 2,161,560, June 6, 1939. M. L. Crossley. A polychlorinated naphthol is used to improve the film strength of lubricating oils.
- U. S. 2,161,584, June 6, 1939. R. C. Moran and E. W. Fuller. Diethyl xanthyl ethyl ether is used to improve the film strength of lubricating oils.
- U. S. 2,161,615, June 6, 1939. M. A. Dietrich. Ethyl oleyl carbamate is used to improve the film strength of lubricating oils.
- U. S. 2,161,678, June 6, 1939. K. H. Klipstein. Dinaphthyl or dixyl dichloroethylene is used to improve the film strength of lubricating oils.
- U. S. 2,162,207, June 13, 1939. R. C. Moran and W. H. James. Dianiline disulfide is used to prevent corrosiveness of lubricating oils.
- U. S. 2,162,398, June 13, 1939. F. C. Haas. Sulfurized sperm oil is used to prevent sludging of lubricating oils in service.
- U. S. 2,163,535, June 20, 1939. H. G. Berger, R. C. Moran, and F. M. Seger. Petroleum naphtha is chlorinated and dissolved in acetone, and the solution reacted with an alkali alkyl thiocarbamate. The product is used to improve film strength of lubricating oils.
- U. S. 2,164,393, July 4, 1939. E. A. Evans. Film strength of lubricating oils is improved by the addition of 3-carbomethoxy-4-hydroxyphenol.
- U. S. 2,166,286, July 18, 1939. R. B. Denham. Halogenated lecithin is used to improve the film strength of lubricating oils.
- U. S. 2,167,064, July 25, 1939. M. A. Dietrich. A reaction product of cracked gases and a halogenated decahydronaphthalene is used to improve the viscosity index of lubricating oils.
- U. S. 2,167,867, Aug. 1, 1939. A. F. Benning. Tritolyl phosphate is used to prevent corrosiveness of lubricating oils.
- U. S. 2,168,262, Aug. 1, 1939. E. N. Klemgard and V. L. Ricketts. An iso-

- amyl ester of benzene mono- or disulfonic acid is used to improve the film strength of lubricating oils.
- U. S. 2,168,666, Aug. 8, 1939. M. R. Cannon. A reaction product of urea and a sulfonated oil is used to reduce the corrosiveness of lubricating oils.
- U. S. 2,168,674, Aug. 8, 1939. C. M. Loane and B. H. Shoemaker. Octyl isocyanate, phenyl isocyanate, octyl cyanide, or benzonitrile is used to reduce corrosiveness of lubricating oils.
- U. S. 2,168,848, Aug. 8, 1939. A. W. Ralston. Heptadecylthioamide is used to improve the film strength of lubricating oils.
- U. S. 2,169,155, Aug. 8, 1939. B. H. Lincoln and A. Henriksen. Calcium, lead, or aluminum salt of a chlorinated naphthenic acid is used to improve the film strength of lubricating oils.
- U. S. 2,169,185, Aug. 8, 1939. B. H. Shoemaker and C. M. Loane. Tri-beta-chloropropyl phosphite is used to reduce the corrosiveness of lubricating oils.
- U. S. 2,169,634, Aug. 15, 1939. T. L. Cantrell and J. O. Turner. Film strength of lubricating oils is improved by the addition of a condensation product of butylene and phenol which has been treated with sulfide of phosphorus.
- U. S. 2,169,700, Aug. 15, 1939. C. M. Loane and B. H. Shoemaker. Dodecene dithiocyanate is used to improve the film strength of lubricating oils.
- U. S. 2,172,285, Sept. 5, 1939. B. H. Lincoln and W. L. Steiner. Film strength of lubricating oils is improved with a sulfonated wool oil.
- U. S. 2,172,382, Sept. 12, 1939. A. Henriksen and B. H. Lincoln. A condensation product of chlorinated wax and naphthalene is used to reduce the pour point and improve the film strength of lubricating oils.
- U. S. 2,172,954, Sept. 12, 1939. F. M. Clark. Tetrachlorodiphenyl sulfide is used to improve the film strength of lubricating oils.
- U. S. 2,173,117, Sept. 19, 1939. J. W. Johnson, Jr. Naphthenic acid ester of diethylene glycol mono-butyl ether is used to improve the oiliness of lubricating oils.
- U. S. 2,174,019, Sept. 26, 1939. F. W. Sullivan, Jr. Diethyl isoamyl thiophosphinite and similar substances are used to inhibit corrosiveness of lubricating oils.
- U. S. 2,177,561, Oct. 24, 1939. E. W. Cook. Triphenylstibine is used to reduce corrosiveness of lubricating oils.
- U. S. 2,178,610, Nov. 7, 1939. P. L. Salzberg. Trinaphthenyl trithiophosphite is used to reduce the corrosiveness of lubricating oils.
- U. S. 2,180,008, Nov. 14, 1939. B. H. Lincoln, W. L. Steiner, and A. Henriksen. Chlorinated resorcinol is used to improve the film strength of lubricating oils.
- U. S. 2,184,944, Dec. 26, 1939. A. J. van Peski. The liquid sulfur dioxide extract of oil is hydrogenated to eliminate olefins, and the resulting product rich in aromatic hydrocarbons is added to lubricating oils to improve their stability.
- U. S. 2,185,009, Dec. 26, 1939. J. H. Babcock and A. Loverde. Dichlorophenyl methyl polysulfide, dichloronaphthyl methyl polysulfide, dichloroanthracyl methyl polysulfide and similar compounds are used to improve the film strength of lubricating oils.
- U. S. 2,225,197, Dec. 17, 1940. B. A. Stagner. Metal-alkoxide-carboxylates as addition agents to improve the performance and chemical stability of lubricating oils.
- U. S. 2,248,848, July 8, 1941. R. Bulkley, L. A. Hamilton, and V. A. Kalichevsky. Stabilizing lubricating oils against oxidation and acid formation by adding not over 0.5% of sulfonic acids formed from treating lubricating oils.



Appendix

SPECIAL TABLES

Table 115. Centigrade-Fahrenheit Conversion Table.

°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.
0	32	50	122	100	212	150	302	200	392	250	482	300	572	350	662
1	34	1	124	1	214	1	304	1	394	1	484	1	574	60	680
2	36	2	126	2	216	2	306	2	396	2	486	2	576	70	698
3	37	3	127	3	217	3	307	3	397	3	487	3	577	80	716
4	39	4	129	4	219	4	309	4	399	4	489	4	579	90	734
5	41	5	131	5	221	5	311	5	401	5	491	5	581	400	752
6	43	6	133	6	223	6	313	6	403	6	493	6	583	10	770
7	45	7	135	7	225	7	315	7	405	7	495	7	585	20	788
8	46	8	136	8	226	8	316	8	406	8	496	8	586	30	806
9	48	9	138	9	228	9	318	9	408	9	498	9	588	40	824
10	50	60	140	110	230	160	320	210	410	260	500	310	590	50	842
1	52	1	142	1	232	1	322	1	412	1	502	1	592	60	860
2	54	2	144	2	234	2	324	2	414	2	504	2	594	70	878
3	55	3	145	3	235	3	325	3	415	3	505	3	595	80	896
4	57	4	147	4	237	4	327	4	417	4	507	4	597	90	914
5	59	5	149	5	239	5	329	5	419	5	509	5	599	500	932
6	61	6	151	6	241	6	331	6	421	6	511	6	601	10	950
7	63	7	153	7	243	7	333	7	423	7	513	7	603	20	968
8	64	8	154	8	244	8	334	8	424	8	514	8	604	30	986
9	66	9	156	9	246	9	336	9	426	9	516	9	606	40	1004
20	68	70	158	120	248	170	338	220	428	270	518	320	608	50	1022
1	70	1	160	1	250	1	340	1	430	1	520	1	610	60	1040
2	72	2	162	2	252	2	342	2	432	2	522	2	612	70	1058
3	73	3	163	3	253	3	343	3	433	3	523	3	613	80	1076
4	75	4	165	4	255	4	345	4	435	4	525	4	615	90	1094
5	77	5	167	5	257	5	347	5	437	5	527	5	617	600	1112
6	79	6	169	6	259	6	349	6	439	6	529	6	619	10	1130
7	81	7	171	7	261	7	351	7	441	7	531	7	621	20	1148
8	82	8	172	8	262	8	352	8	442	8	532	8	622	30	1166
9	84	9	174	9	264	9	354	9	444	9	534	9	624	40	1184
30	86	80	176	130	266	180	356	230	446	280	536	330	626	50	1202
1	88	1	178	1	268	1	358	1	448	1	538	1	628	60	1220
2	90	2	180	2	270	2	360	2	450	2	540	2	630	70	1238
3	91	3	181	3	271	3	361	3	451	3	541	3	631	80	1256
4	93	4	183	4	273	4	363	4	453	4	543	4	633	90	1276
5	95	5	185	5	275	5	365	5	455	5	545	5	635	700	1292
6	97	6	187	6	277	6	367	6	457	6	547	6	637	10	1310
7	99	7	189	7	279	7	369	7	459	7	549	7	639	20	1328
8	100	8	190	8	280	8	370	8	460	8	550	8	640	30	1346
9	102	9	192	9	282	9	372	9	462	9	552	9	642	40	1364
40	104	90	194	140	284	190	374	240	464	290	554	340	644	50	1382
1	106	1	196	1	286	1	376	1	466	1	556	1	646	60	1400
2	108	2	198	2	288	2	378	2	468	2	558	2	648	70	1418
3	109	3	199	3	289	3	379	3	469	3	559	3	649	80	1436
4	111	4	201	4	291	4	381	4	471	4	561	4	651	90	1454
5	113	5	203	5	293	5	383	5	473	5	563	5	653	800	1472
6	115	6	205	6	295	6	385	6	475	6	565	6	655	10	1490
7	117	7	207	7	297	7	387	7	477	7	567	7	657	20	1508
8	118	8	208	8	298	8	388	8	478	8	568	8	658	30	1526
9	120	9	210	9	300	9	390	9	480	9	570	9	660	40	1544

Table 116. Degrees A.P.I., Specific Gravities, and Pounds per Gallon at 60° F.
(Liquids Lighter Than Water).^a

Degrees A.P.I.	Specific Gravity at 60°/60° F.	Pounds per Gallon at 60° F. ^b	Degrees A.P.I.	Specific Gravity at 60°/60° F.	Pounds per Gallon at 60° F. ^b
0.....	1.0760	8.962	50.....	0.7796	6.490
1.....	1.0679	8.895	51.....	0.7753	6.455
2.....	1.0599	8.828	52.....	0.7711	6.420
3.....	1.0520	8.762	53.....	0.7669	6.385
4.....	1.0443	8.698	54.....	0.7628	6.350
5.....	1.0366	8.634	55.....	0.7587	6.316
6.....	1.0291	8.571	56.....	0.7547	6.283
7.....	1.0217	8.509	57.....	0.7507	6.249
8.....	1.0143	8.448	58.....	0.7467	6.216
9.....	1.0071	8.388	59.....	0.7428	6.184
10.....	1.0000	8.328	60.....	0.7389	6.151
11.....	0.9930	8.270	61.....	0.7351	6.119
12.....	0.9861	8.212	62.....	0.7313	6.087
13.....	0.9792	8.155	63.....	0.7275	6.056
14.....	0.9725	8.099	64.....	0.7238	6.025
15.....	0.9659	8.044	65.....	0.7201	5.994
16.....	0.9593	7.989	66.....	0.7165	5.964
17.....	0.9529	7.935	67.....	0.7128	5.934
18.....	0.9465	7.882	68.....	0.7093	5.904
19.....	0.9402	7.830	69.....	0.7057	5.874
20.....	0.9340	7.778	70.....	0.7022	5.845
21.....	0.9279	7.727	71.....	0.6988	5.817
22.....	0.9218	7.676	72.....	0.6953	5.788
23.....	0.9159	7.627	73.....	0.6919	5.759
24.....	0.9100	7.578	74.....	0.6886	5.731
25.....	0.9042	7.529	75.....	0.6852	5.703
26.....	0.8984	7.481	76.....	0.6819	5.676
27.....	0.8927	7.434	77.....	0.6787	5.649
28.....	0.8871	7.387	78.....	0.6754	5.622
29.....	0.8816	7.341	79.....	0.6722	5.595
30.....	0.8762	7.296	80.....	0.6690	5.568
31.....	0.8708	7.251	81.....	0.6659	5.542
32.....	0.8654	7.206	82.....	0.6628	5.516
33.....	0.8602	7.163	83.....	0.6597	5.491
34.....	0.8550	7.119	84.....	0.6566	5.465
35.....	0.8498	7.076	85.....	0.6536	5.440
36.....	0.8448	7.034	86.....	0.6506	5.415
37.....	0.8398	6.993	87.....	0.6476	5.390
38.....	0.8348	6.951	88.....	0.6446	5.365
39.....	0.8299	6.910	89.....	0.6417	5.341
40.....	0.8251	6.870	90.....	0.6388	5.316
41.....	0.8203	6.830	91.....	0.6360	5.293
42.....	0.8155	6.790	92.....	0.6331	5.269
43.....	0.8109	6.752	93.....	0.6303	5.246
44.....	0.8063	6.713	94.....	0.6275	5.222
45.....	0.8017	6.675	95.....	0.6247	5.199
46.....	0.7972	6.637	96.....	0.6220	5.176
47.....	0.7927	6.600	97.....	0.6193	5.154
48.....	0.7883	6.563	98.....	0.6166	5.131
49.....	0.7839	6.526	99.....	0.6139	5.109
			100.....	0.6112	5.086

^a This table is taken from page 255 of the Report of the Committee D-2 of the American Society for Testing Materials, for 1930.

^b The data in this column are based upon apparent weights in air, the weight of one gallon of water at 60° F. in air being assumed to be 8.32828 lb. Consequently, a correction for the buoyancy of air is required in computing these figures from the specific gravities in the second column.

Table 17. Sodium Hydroxide (Caustic Soda) Solution at 15° C. (59° F.) (Lunge).

Specific Gravity	Degrees Baumé	Degrees Twaddell	Per Cent NaOH	Grams NaOH per Liter
1.007	1.0	1.4	0.61	6
1.014	2.0	2.9	1.20	12
1.022	3.1	4.4	2.00	21
1.029	4.1	5.8	2.70	28
1.036	5.1	7.2	3.35	35
1.045	6.2	9.0	4.00	42
1.052	7.2	10.4	4.64	49
1.060	8.2	12.0	5.29	56
1.067	9.1	13.4	5.87	63
1.075	10.1	15.0	6.55	70
1.083	11.1	16.6	7.31	79
1.091	12.1	18.2	8.00	87
1.100	13.2	20.0	8.68	95
1.108	14.1	21.6	9.42	104
1.116	15.1	23.2	10.06	112
1.125	16.1	25.0	10.97	123
1.134	17.1	26.8	11.84	134
1.142	18.0	28.4	12.64	144
1.152	19.1	30.4	13.55	156
1.162	20.2	32.4	14.37	167
1.171	21.2	34.2	15.13	177
1.180	22.1	36.0	15.91	188
1.190	23.1	38.0	16.77	200
1.200	24.2	40.0	17.67	212
1.210	25.2	42.0	18.58	225
1.220	26.1	44.0	19.58	239
1.231	27.2	46.2	20.59	253
1.241	28.2	48.2	21.42	266
1.252	29.2	50.4	22.64	283
1.263	30.2	52.6	23.67	299
1.274	31.2	54.8	24.81	316
1.285	32.2	57.0	25.80	332
1.297	33.2	59.4	26.83	348
1.308	34.1	61.6	27.80	364
1.320	35.2	64.0	28.83	381
1.332	36.1	66.4	29.93	399
1.345	37.2	69.0	31.22	420
1.357	38.1	71.4	32.47	441
1.370	39.2	74.0	33.69	462
1.383	40.2	76.6	34.96	483
1.397	41.2	79.4	36.25	506
1.410	42.2	82.0	37.47	528
1.424	43.2	84.8	38.80	553
1.438	44.2	87.6	39.99	575
1.453	45.2	90.6	41.41	602
1.468	46.2	93.6	42.83	629
1.483	47.2	96.6	44.38	658
1.498	48.2	99.6	46.15	691
1.514	49.2	102.8	47.60	721
1.530	50.2	106.0	49.02	750



Table 118. Sulfuric Acid.
(Close approximation.)

Strength % H ₂ SO ₄	Baumé Gravity 60°/60° F.	Specific Gravity 60°/60° F.	Boiling Point °C.	Grams H ₂ SO ₄ per 100 cc. of Acid	Cc. of H ₂ O to Add to 100 cc. of 93.1% Acid	Cc. per Liter Equivalent to 1 lb. of Acid per Barrel	1 lb. Actual H ₂ SO ₄ per Barrel
40	34.1	1.3090	114	52	243	2.17	5.50
43	36.3	1.3337	117	57	212	2.14	5.01
45	37.8	1.3519	118	60	196	2.11	4.76
48	40.0	1.3800	122	66	172	2.06	4.33
50	41.4	1.3993	124	70	158	2.04	4.09
53	43.5	1.4016	128	76	138	2.01	3.76
55	45.0	1.4476	132	80	127	1.97	3.57
58	47.1	1.4833	138	86	111	1.93	3.32
60	48.5	1.5075	141	90	101	1.89	3.18
63	50.6	1.5253	148	97	88	1.87	2.95
65	51.9	1.5576	153	101	79	1.83	2.83
68	53.9	1.5919	162	109	68	1.79	2.62
70	55.2	1.6153	170	114	61	1.76	2.51
73	57.2	1.6507	178	121	51	1.73	2.36
75	58.4	1.6720	185	126	44	1.70	2.27
78	60.2	1.7078	199	135	35	1.67	2.12
80	61.3	1.7390	207	140	30	1.64	2.03
83	62.8	1.7648	223	147	23	1.61	1.94
85	63.7	1.7839	233	152	18	1.59	1.88
88	64.8	1.8081	251	159	11	1.58	1.80
90	65.3	1.8201	262	164	6	1.57	1.74
93	66.0	1.8346	281	171	0	1.56	1.67
103.3% Acid							
95	66.2	1.8390	295	173	16	1.55	1.65
98	66.3	1.8409	293	179	10	1.55	1.60
100	66.2	1.8384	290	184	6	1.55	1.55
103	69.4	1.9180	...	192	0	1.49	1.44

Table 119. Volumetric Dilution of Sulfuric Acid.

Strength of Original Acid (%)	40	Strength of the Diluted Acid (%)												
		(Formed by adding 45 cc. of water to 100 cc. of original acid)	50	55	60	65	70	75	80	85	90	95	100	
40	0	
45	16	
50	35	15	
55	55	32	14	
60	75	50	30	15	
65	97	68	47	28	12	
70	121	88	65	44	26	12	
75	146	111	84	61	42	25	12	
80	173	135	104	79	58	40	25	11	
85	200	158	125	97	74	55	38	24	11	
90	227	182	145	115	91	70	52	36	23	11	
95	251	202	164	132	106	84	65	49	34	22	10	
100	276	224	184	151	122	99	79	62	46	33	20	9	..	

The figures in the table denote the volume of water to be added to 100 volumes of the original acid to yield the desired strength.
Example—Original acid of 95% strength is diluted to acid of 80% strength by adding 34 volumes of water to 100 volumes of the 95% acid.

Table 120. Grams per Liter to Pounds per Barrel.^a
 (1 gram per liter = 0.35049 lb. per barrel of 42 gal.)

Grams per Liter	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0.00	0.03	0.07	0.10	0.14	0.17	0.21	0.24	0.28	0.31
1	0.35	0.38	0.42	0.45	0.49	0.53	0.56	0.60	0.63	0.67
2	0.70	0.74	0.77	0.80	0.84	0.88	0.91	0.95	0.98	1.01
3	1.05	1.09	1.12	1.16	1.19	1.23	1.26	1.30	1.33	1.37
4	1.40	1.44	1.47	1.50	1.54	1.58	1.61	1.65	1.68	1.72
5	1.75	1.79	1.82	1.86	1.89	1.93	1.96	2.00	2.03	2.07
6	2.10	2.14	2.17	2.20	2.24	2.28	2.31	2.35	2.38	2.41
7	2.45	2.49	2.52	2.56	2.59	2.63	2.66	2.70	2.73	2.77
8	2.80	2.84	2.87	2.90	2.95	2.98	3.01	3.05	3.08	3.11
9	3.15	3.19	3.22	3.26	3.29	3.33	3.36	3.40	3.43	3.47

Pounds per Barrel to Grams per Liter.^a
 (1 lb. per barrel = 2.8531 grams per liter.)

Lbs. per Bbl.	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0.00	0.28	0.57	0.86	1.14	1.43	1.71	2.00	2.28	2.57
1	2.85	3.14	3.42	3.71	4.00	4.28	4.56	4.85	5.14	5.42
2	5.70	5.99	6.28	6.56	6.85	7.13	7.41	7.70	7.99	8.27
3	8.56	8.84	9.13	9.41	9.70	9.99	10.27	10.56	10.84	11.13
4	11.41	11.70	11.98	12.27	12.55	12.84	13.12	13.41	13.69	13.98
5	14.27	14.55	14.84	15.12	15.41	15.69	15.98	16.26	16.55	16.83
6	17.12	17.40	17.69	17.97	18.26	18.55	18.83	19.11	19.40	19.69
7	19.97	20.26	20.54	20.83	21.11	21.40	21.68	21.97	22.25	22.54
8	22.82	23.11	23.40	23.68	23.97	24.25	24.54	24.82	25.11	25.39
9	25.68	25.96	26.25	26.53	26.82	27.10	27.39	27.68	27.96	28.25

^a See next to last column of Table 66 for corresponding conversion figures for cc. of sulfuric acid per liter and pounds per barrel.

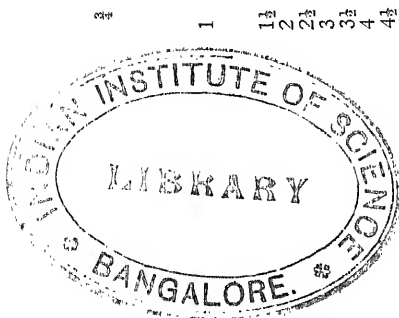
Table 121. Approximate Color Conversion Table.¹

Saybolt Color	Stamper Color	Wilson Grade	N.P.A. (A.S.T.M.) Color	N.P.A. Name	Union Color	Tag- Robinson Color	Lovibond Color (3" cell)	"True" Color
30								0.0128
29								0.0142
28								0.0160
27								0.0183
26								0.0213
25		1						0.0256
24	310							0.0284
23	280	1½						0.0320
23	253							0.0366
22	226	2						0.0426
21	199			Water-White				0.0476
20	184	2¼						0.0539
19	166							0.0621
18	143							0.0706
17	127							0.0819
16	107	2¾						0.0976
15	86½	3		Prime White				0.105
14	81							0.114
13	76							0.124
12	68	3½						0.132
11	63							0.141
10	57							0.152
9	50	4						0.158
8								0.164
7								0.171
6								0.178
5								0.186
4								0.195
3			½					0.205
2								0.216
1								0.228
0				Standard White				0.241
-1								0.256
-2			¾					0.273
-3								0.283
-4								

1	Lily White	G	21	0.4	0.293
1½	Cream White	H	17.5	1.5	0.303
2	Extra Pale	I	12.5	5.5	0.315
2½	Extra Lemon Pale	J	10.25	10	0.328
3	Lemon Pale	K	9.75	14	0.341
3½	Extra Orange Pale	L	9.25	20	0.356
4	Orange Pale	M	8.25	32	0.372
4½	Pale	N	5.75	42	0.390
5	Light Red	O	3.50	55	0.410
6	Dark Red	P	2.25	90	0.431
7	Claret Red	Q	2.25	135	0.455
8	Extra Dark Red	R	1.50	200	0.482
A	Extra Light Filtered	A	0.90		1.5
D	Light Filtered	D			5.5
E	Medium Filtered	E			10

¹ Exact color comparisons are impossible for reasons explained on page 249.

² Corrected for dilution (15 oil: 85 water-white kerosene). Calculated from iodimetric colors given by Cross, Handbook of Petroleum, Asphalt, and Natural Gas, 1924.



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Table 122. Classification of Lubricants.
(S.A.E. Recommended Practice)

Crankcase Oils

S.A.E. Viscosity Number	Viscosity Range (Saybolt Universal Seconds)			
	at 130° F.		at 210° F.	
	(Min.)	(Max.)	(Min.)	(Max.)
10	90	<120
20	120	<185
30	185	<255
40	255	< 80
50	80	<105
60	105	<125
70	125	<150

Transmission and Rear-Axle Lubricants

S.A.E. Viscosity Number	Viscosity Range (Saybolt Universal Seconds)	Consistency, Must Not Channel in Service (°F.)
80	100,000 at 0° F. Max.	-20
90	800-1500 at 100° F.	0
140	120-200 at 210° F.	+35
250	200 at 210° F. Min.	..

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<i>Belgian</i>	
152,278	242
179,502	239
347,671	149

<i>Brazilian</i>	
5,667	115

<i>British</i>	
475 (1911)	116
610 (1868)	311
648 (1868)	311
966 (1770)	114
1,211 (1855)	307
1,664 (1898)	241
1,864 (1792)	116
1,878 (1914)	177
2,356 (1868)	310
2,410 (1879)	243
2,721 (1867)	307
3,020 (1870)	114
3,572 (1914)	241, 396
3,942 (1873)	310
4,574 (1914)	307
4,769 (1877)	240
5,132 (1889)	240
5,208 (1883)	306
6,825 (1912)	114
7,142 (1890)	310
7,808 (1898)	309
8,077 (1912)	177
8,486 (1906)	176
9,856 (1912)	396
10,004 (1903)	241
10,139 (1885)	307
10,968 (1886)	239
11,140 (1908)	338
11,893 (1905)	176
12,230 (1907)	116
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15,036 (1907)	117
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16,617 (1908)	308
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17,440 (1907)	239
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20,077 (1913)	177
20,649-50 (1910)	311
20,879 (1898)	150
22,147 (1914)	240
23,324 (1908)	311
23,368 (1910)	151
24,216 (1909)	239
25,496 (1911)	177
25,510 (1913)	307
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300,900	241
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301,450	115
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313,523	177
314,052	116
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315,809	114
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316,274	338
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319,718	149
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321,200	115
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110,054	434	444,833	434	716,132	429
112,453	487	448,480	240	721,426	307
113,782	117	451,660	434	722,506	426
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120,349	115	452,578	434	723,368	239
120,631	487	454,061	309	732,937	429
127,446	417	470,911	434	736,479	430
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133,425	115	487,119	176	747,347	176
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138,629	240	488,628	150	761,939	176
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160,759	426	495,124	417	783,916	119
161,672	307	495,343	426	793,026	239
164,117	487	498,588	417	807,983	117
167,730	487	500,252	240	809,086	239
170,581	488	501,988	239	809,087	435
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176,423	114	507,441	429	837,655	435
178,061	426	518,989	115	850,898	176
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186,951	119	523,716	242	898,879	449
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237,484	307	556,155	435	923,427	150
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240,937	117	559,783	417	929,503	474
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345,872	311	623,066	418	1,018,971	488
359,357	116	625,332	426	1,042,915	116
370,950	238	640,918	435	1,057,395	149
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378,246	240	651,474	306	1,063,870	426
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389,898	434	658,857	116	1,070,435	449
400,633	114	664,017	449	1,073,233	430
407,182	240	664,408	311	1,075,481	449
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413,187	434	671,135	426	1,092,386	426
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1,303,779	149	1,438,764	177	1,552,072	309
1,309,206	150	1,438,985	176	1,552,830	240
1,309,432	239	1,439,171	177	1,553,141	430
1,310,164	117	1,440,286	307	1,558,162-3	308
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1,319,129	488	1,450,617	430	1,562,156	176
1,320,396	117	1,451,052	436	1,562,425	458
1,324,649	309	1,454,593	430	1,563,012	114
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1,326,072	435	1,457,656	307	1,568,812-3	240
1,330,624	149	1,459,084	149	1,568,886	239
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1,356,631	449	1,471,201	310	1,570,005	310
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1,575,905	240	1,650,782	311	1,698,428	239
1,577,723	150	1,651,328	458	1,698,432	115
1,577,852	310	1,652,399	114	1,698,471	117
1,577,852	117	1,652,813	365	1,699,989	450
1,579,326	450	1,653,735	310	1,700,479	308
1,579,607	150	1,654,581	436	1,702,313	116
1,580,531	242	1,655,068	436	1,703,158	418
1,581,369	436	1,655,069	396	1,703,615	115
1,581,370	311	1,655,175	306	1,703,616	437
1,585,473	458	1,655,890	306	1,703,838	418
1,585,922	308	1,656,990	118	1,704,206	117
1,586,801	150	1,656,997	306	1,704,246	437
1,587,491	309	1,658,285	396	1,705,199	116
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1,594,041	117	1,662,323	365	1,706,940	149
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1,604,235	242	1,668,920	117	1,714,133	339
1,604,641	150	1,669,181	243	1,715,095	430
1,605,046	177	1,671,721	116	1,715,535	450
1,608,089	307	1,672,304	242	1,716,632	307
1,608,135	306	1,672,621	242	1,716,973	437
1,608,328	436	1,673,045	427	1,716,974	310
1,608,329	242	1,674,676	458	1,718,218	437
1,608,339	436	1,676,294	242	1,718,335	150
1,609,349	436	1,676,724	239	1,718,375	177
1,614,660	307	1,677,425	114	1,718,672	450
1,615,286	309	1,677,440	116	1,718,713	242
1,616,352	115	1,677,731	151	1,718,714	430
1,616,353	114	1,678,298	308	1,719,177	150
1,617,201	418	1,678,299	308	1,719,180	150
1,617,476	307	1,678,984	241	1,719,762	150
1,621,071	427	1,679,093	118	1,720,144	310
1,621,475	114, 115	1,679,214	118	1,724,531	310
1,622,228	365	1,680,352	458	1,725,068	115
1,622,233	365	1,681,638	116	1,725,320	418
1,622,671	242	1,681,657	176	1,725,611-2	118
1,622,879	242	1,682,562	241	1,725,921	117
1,623,018	436	1,682,603	307	1,728,059	117
1,624,692	310	1,682,639	427	1,728,156	430
1,625,195	115	1,682,713	427	1,729,782	116
1,625,415	118	1,683,193	308	1,729,943	241
1,627,055	239	1,683,288	458	1,731,716	150
1,627,338	242	1,683,767	458	1,732,371	458
1,628,423	242	1,684,035	308	1,732,465	114
1,628,747	450	1,684,159	243	1,732,905	430
1,631,401	338	1,684,489	116	1,733,545	114
1,633,871	450	1,684,868	118	1,733,597	117
1,635,216	365	1,685,034	436	1,733,656	437
1,635,718	116	1,685,681	310	1,733,619	118
1,636,724	427	1,686,136	116	1,733,620	177
1,636,938	308	1,686,491	430	1,733,800	241
1,636,946	418	1,686,493	308	1,734,197	306
1,638,643-4	310	1,687,992	436	1,734,959	450
1,639,531	177	1,690,772	307	1,735,988	309
1,639,988	115	1,691,266	436	1,736,018	114
1,640,720	242	1,692,756	241	1,736,022	309
1,641,520	364	1,693,207	310	1,736,234	309
1,641,546	309	1,694,268	365	1,738,070	458
1,642,060	427	1,694,463	176	1,738,330	177
1,643,272	488	1,694,478	430	1,738,518	430
1,645,530	396	1,694,971	307	1,739,734	309
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2,011,199	118	2,028,905	456	2,044,996	118, 461
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2,012,356	476	2,029,005	432	2,045,160	456
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2,013,083	455	2,029,115	423	2,045,262	445
2,013,198	484	2,029,256	485	2,045,492	433
2,013,293	444	2,029,748	485	2,045,696	461
2,013,399	422	2,029,757	485	2,046,907	485
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2,013,663	461	2,029,785	423	2,047,355	485
2,014,300	484	2,030,033	485	2,047,380	461
2,014,235	479	2,030,245	433	2,047,475	433
2,014,556	428	2,030,940	485	2,047,755	461
2,014,923	484	2,031,117	461	2,047,985	423
2,014,924	479	2,031,917	485	2,048,169	445
2,015,038	444	2,031,930	479	2,048,241	445
2,015,080	444	2,031,939	423	2,048,521	423
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2,017,756	484	2,033,942	461	2,050,345	423
2,018,570	476	2,034,068	445	2,050,732	485
2,018,715	423	2,034,197	433	2,050,772	445
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2,053,421	486	2,074,183	433	2,085,521	463
2,053,457	462	2,074,467	486	2,085,523	447
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2,055,810	479	2,078,882	429	2,087,048	242, 457
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2,056,978	486	2,079,424	429	2,087,582	477
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2,071,064	486	2,084,510	457	2,097,440	429
2,071,590	462	2,084,512	463	2,097,729	464
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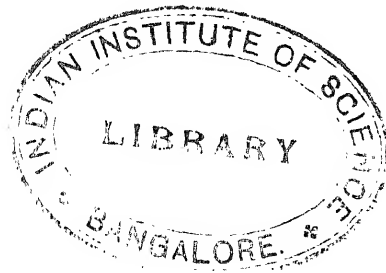
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2,099,190	464	2,111,822	466	2,123,205	467
2,099,529	424	2,111,864	466	2,123,457	481
2,099,835	424	2,111,920	429	2,123,503	424
2,100,070	464	2,111,957	466	2,123,641	491
2,100,099	464	2,111,968	466	2,123,833	467
2,100,429	464	2,111,990	490	2,123,982	467
2,100,685	480	2,112,109	490	2,124,531	467
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2,100,915	464	2,112,313	433	2,124,606	467
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2,102,878	395	2,114,313	447	2,126,055	467
2,103,504	461	2,114,352	424	2,126,493	467
2,104,049	480	2,114,354	447	2,126,503	242
2,104,097	490	2,114,437	480	2,126,590	491
2,104,379	464	2,114,467	466	2,126,867	424
2,104,401	465	2,114,524	466	2,127,325	467
2,104,791	447	2,114,525	491	2,127,654	457
2,104,796	480	2,114,812	466	2,127,708	467
2,105,464	447	2,114,852	447	2,128,029	467
2,105,523	433	2,115,003	466	2,128,109	467
2,106,071	457	2,115,063	448	2,128,574	491
2,106,232	490	2,115,341	491	2,128,885	467
2,106,234	465	2,115,354	491	2,128,910	477
2,106,247	465	2,115,355	480	2,128,931	457
2,106,554	490	2,115,401	466	2,128,958	467
2,106,767	490	2,115,704	466	2,129,281	491
2,106,960	465	2,115,781	480	2,129,282	467
2,106,964	465	2,115,823	466	2,129,616	467
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2,107,215	457	2,116,188	466	2,131,138	491
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2,107,354	457	2,116,220	457	2,131,519	448
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2,107,713	434	2,116,540	466	2,131,879	424
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2,107,771	465	2,117,076	491	2,131,999	468
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2,107,807	465	2,118,214-7	491	2,132,150	468
2,107,905	490	2,118,310	457	2,132,151	468
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2,108,629	465	2,119,097	491	2,132,359	468
2,108,636	465	2,119,114	480	2,132,847	491
2,108,690	457	2,119,149	491	2,132,968	477
2,108,954	480	2,119,240	424	2,133,094	434
2,109,125	465	2,119,403	491	2,133,452	425
2,109,130	465	2,119,556	491	2,133,457	425
2,109,157	465	2,119,718	466	2,133,493	491
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2,109,357	490	2,119,759	466	2,133,691	468
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2,109,463	465	2,119,940	467	2,134,336	468
2,109,476	490	2,120,135	424	2,134,337	468
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2,136,885	468	2,145,852	425	2,154,189	471
2,137,080	477	2,145,889	477	2,154,372	471
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2,137,209	468	2,146,584	493	2,155,204	471
2,137,218	468	2,146,650	469	2,155,644	471
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2,137,544	468	2,147,155	493	2,155,678	481
2,137,727	492	2,147,222	470	2,156,158	481
2,137,777	492	2,147,315	470	2,156,577	448
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2,137,783	492	2,147,546	470	2,157,078	493
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2,138,566	448	2,147,573	470	2,157,224	477
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2,138,835	492	2,148,056	434	2,157,879	150
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2,139,335	492	2,149,221	477	2,158,671	471
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2,142,998	425	2,151,592	471	2,161,585	481
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2,143,142	492	2,151,721	448	2,161,678	494
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2,143,872	469	2,152,721	448	2,162,208	481
2,143,882	469	2,152,722	448	2,162,319	457
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2,164,393	494	2,168,848	495	2,176,883	482
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2,166,286	494	2,172,285	495	2,181,036-7	449
2,166,502	435	2,172,320	473	2,181,121	482
2,166,503	425	2,172,382	495	2,181,122	482
2,166,544	478	2,172,436	458	2,181,638	473
2,167,064	494	2,172,954	495	2,183,801	243
2,167,273	481	2,173,117	495	2,184,838	474
2,167,340	472	2,173,915	473	2,184,944	495
2,167,602	478	2,174,019	495	2,184,956	478
2,167,632	472	2,174,023	434	2,184,961	474
2,167,730	472	2,174,174	473	2,185,009	495
2,167,867	494	2,174,246	473	2,185,291	474
2,167,970	472	2,174,248	481	2,185,311	474
2,168,078	243	2,174,810	449	2,185,577	426
2,168,140	472	2,174,908	425	2,185,768	449
2,168,362	494	2,174,938	473	2,225,197	495
2,168,306	472	2,175,548	482	2,248,848	495
2,168,315	470	2,175,619	482		



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